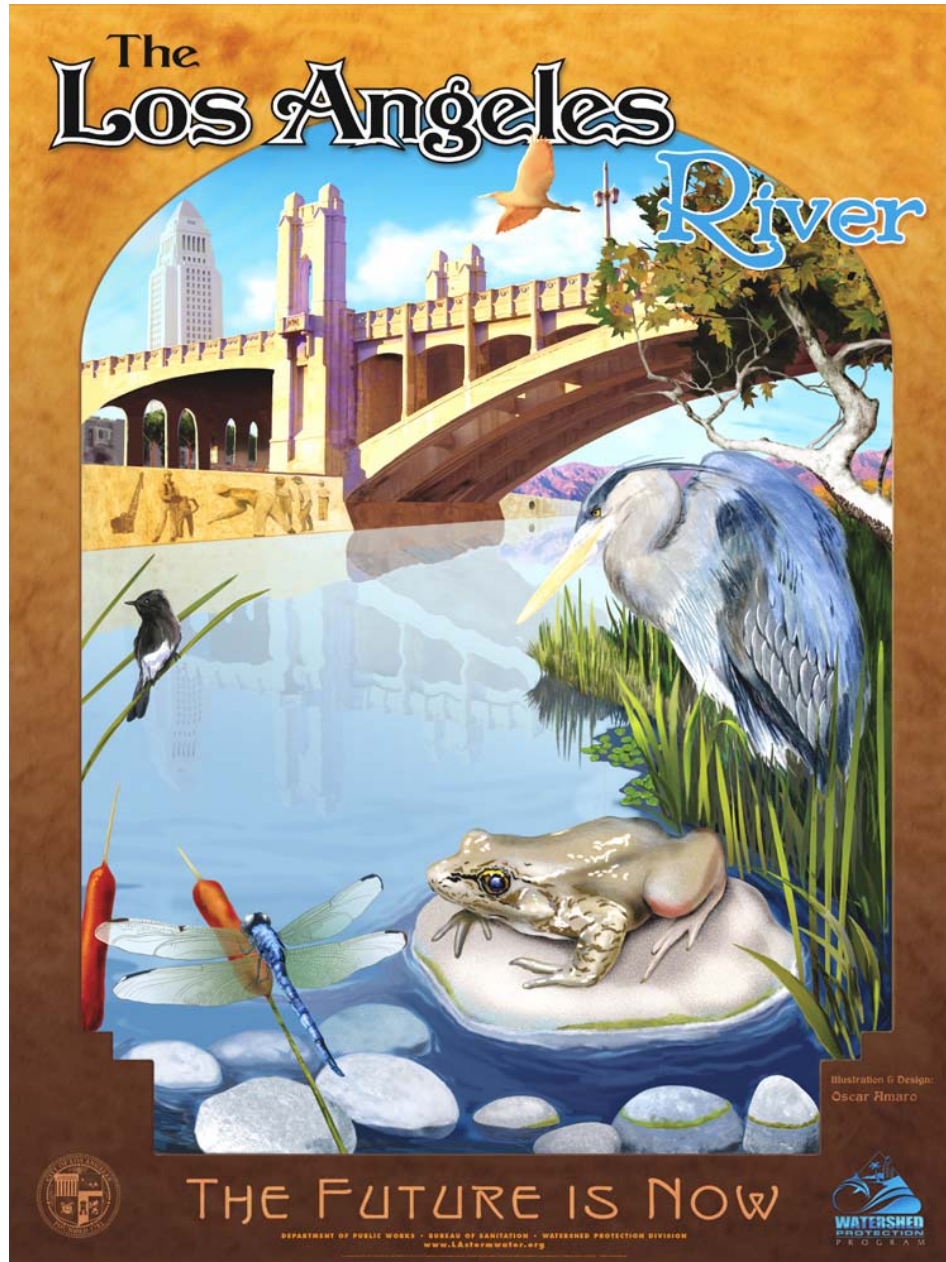


LOS ANGELES RIVER METALS TMDL COORDINATED MONITORING PLAN



**PREPARED BY THE LOS ANGELES RIVER METALS TMDL TECHNICAL
COMMITTEE
CHAIRLED BY THE CITY AND COUNTY OF LOS ANGELES**

APRIL 11, 2007

“SPECIAL THANKS”

Special acknowledgement should be given to the Los Angeles River Technical Committee for the development of this Coordinated Monitoring Plan; specifically the Co-chairs, representing the City and County of Los Angeles, for developing the primary reference materials, and the representatives from the cities of Burbank, Downey, Glendale, Hidden Hills, Irwindale, Long Beach, Pasadena, Signal Hill and Caltrans.

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LIST OF ACRONYMS

µg/L	Microgram per Liter
APHA	American Public Health Association
AWWA	American Water Works Association
BMPs	Best Management Practices
Caltrans	California Department of Transportation
CCD	Charged Coupled Device
cfs	Cubic Feet per Second
CHP	Chemical Hygiene Plan
CLABOS	City of Los Angeles Bureau of Sanitation
CMP	Coordinated Monitoring Plan
COC	Chain-of-Custody
CTR	California Toxics Rule
CWA	Clean Water Act
DMR	Discharge Monitoring Report
ELAP	Environmental Laboratory Accreditation Program
EMC	Even Mean Concentration
EMD	Environmental Monitoring Division
FACT	Fast Automated Curve-fitting Technique
g/day	Gram per day
GIS	Geographic Information System
ICP	Inductively Coupled Plasma
ICSD	Information & Control System Division
LADPW	Los Angeles County Department of Public Work
LAR Metals TMDL	Los Angeles River and Tributaries Metals TMDL
LARWQCB	Los Angeles Regional Water Quality Control Board
LARWMC	Los Angeles River Watershed Management Committee
LIMS	Laboratory Information Management System
mg/kg	Milligram per Kilogram
mg/L	Milligram per Liter
MPH	Mile per Hour
MS4	Municipal Separate Storm Sewer System
NPDES	National Pollutant Discharge Elimination System
PE	Performance Evaluation
POTW	Publicly-Owned Treatment Works
QA/QC	Quality Assurance/Quality Control
RF	Radio Frequency
RPD	Relative Percent Difference
SOP	Standard Operating Procedure
TC	Technical Committee
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
WARM	Warm Freshwater Habitat
WEF	Water Environmental Federation

WILD	Wildlife Habitat
WLAs	Waste Load Allocations
WP	Water Pollution
WPD	Watershed Protection Division

1. EXECUTIVE SUMMARY

Section 303(d) of the 1972 Federal Water Pollution Control Act (Clean Water Act or CWA) mandates that a list of impaired receiving water bodies be developed and maintained for each state, with the California State Water Resources Control Board (SWRCB) adopting 303(d) lists in 1998, 2002, and 2006. Based on a number of critical assumptions, the state may then prioritize and address these impairments through development of Total Maximum Daily Loads (TMDLs) that estimates the load of the constituent(s), which can be assimilated by the water body without inducing the impairment.

The March 22, 1999 Consent Decree between Non-Governmental Organizations (NGOs) and the United States Environmental Protection Agency (USEPA), in consultation with the Los Angeles Regional Water Quality Control Board (LARWQCB), was used to prioritize impaired water bodies, impairment causing constituents, and the TMDL schedule for Los Angeles and Ventura Counties (Refer to Appendix A for more details).

The LARWQCB developed the Los Angeles River and Tributaries Metals TMDL (LAR Metals TMDL) to address potential impairments resulting from the concentrations of Cadmium, Copper, Lead, Selenium and Zinc occasionally exceeding the California Toxics Rule (CTR) standards. The identified beneficial use impairments include wildlife habitat (WILD), rare threatened or endangered species (RARE), warm freshwater habitat (WARM), wetlands (WET), and groundwater recharge (GWR). The TMDL, which became effective on January 11, 2006, has been incorporated as an amendment to the regional Basin Plan. This adopted TMDL requires that the responsible agencies develop a Coordinated Monitoring Plan (CMP) for submission to the LARWQCB by April 11, 2007. The goal of this document is to comply with this LAR Metals TMDL requirement by the required date.

At its July 17, 2006 meeting, the Los Angeles River Watershed Management Committee (LARWMC) recommended formation of a Los Angeles River Metals TMDL Technical Committee (TC) and tasked the group with preparation of this CMP. The monitoring program, which includes both ambient and effectiveness monitoring requirements, will begin as soon as it is practicable after the CMP is approved by the LARWQCB. Consistent with the TMDL, this CMP recognizes six river reaches based jurisdictional groups and proposes a three-tiered monitoring approach to assess jurisdictional attainment of wet and dry weather interim compliance schedules.

Tier I ambient monitoring is a monthly program at nine (9) sites to determine if any of the TMDL identified jurisdictional groups regularly exceed applicable standards based on either wet or dry weather flow criteria. Where low flow channels are present, auto-samplers are proposed for installation, to facilitate the calculation of storm event mean concentrations and mass emission loadings. Tier II effectiveness

monitoring would be instituted at any of seven major tributaries in response to repeated criteria exceedence at the downstream Tier I monitoring site. The intent of this monitoring effort would be to assess both interim dry and wet weather schedule compliance and coarsely subdivide the jurisdictional groups, so that MS4 permittees may effectively participate in the Tier III monitoring effort. Tier III monitoring will focus on direct source control efforts and is expected to be narrowly supported by responsible agencies at the jurisdictional or sub-jurisdictional level or organization.

The analysis for the target constituents will be based on USEPA method 200.7 Inductively Coupled Plasma Atomic Emission Spectrometry (ICP/AES) protocols, which vaporizes both suspended and dissolved sample constituents in a plasma torch, then quantifies total analyte concentrations based on the emission intensity for constituent specific light wavelengths. This method provides adequate detection limits for total metal concentrations of copper, lead and zinc; while other methods (200.8 or SM 3125A) would be applied in reach 6 where selenium is the impairment inducing element. Since particulate and dissolved metals concentrations vary unpredictably with time and flow conditions, the TC proposes to develop a protocol, for LARWQCB staff consideration and approval, recommending detection limit data conversion routines for developing translator values. Once the data handling methodology is formalized, for those samples where total metals concentrations exceed CTR standards, previously filtered sub-samples would be analyzed using the more accurate and expensive USEPA method 200.8 Inductively Coupled Plasma Mass Spectrometry (ICP/MS) to quantify the dissolved fraction. Tier III sampling is expected to encourage filtering to facilitate potential discharge source fingerprinting and control effectiveness.

2. INTRODUCTION

Segments (*i.e.*, reaches) of the Los Angeles River and its tributaries are included on the California 303(d) list of impaired water bodies (LARWQCB, 1998a and 2002) for exceeding the water quality objectives for copper, cadmium, lead, selenium and zinc. The CWA requires that a TMDL then be developed to restore the impaired water bodies to their full beneficial uses.

The LAR Metals TMDL was developed for those reaches identified on the 1998 or 2002 303(d) lists, or where recent data suggested impairments. Metals allocations were developed for upstream reaches and tributaries that drain to impaired reaches. This TMDL complies with 40 CFR 130.2 and 130.7, Section 303(d) of the CWA and USEPA guidance for developing TMDLs in California (USEPA, 2000a). The California Water Code (Porter-Cologne Water Quality Control Act) requires that an implementation plan be developed to achieve water quality objectives.

This CMP is submitted to fulfill the requirement of the LAR Metals TMDL. The entire LAR Metals TMDL documents can be referenced from the LARWQCB website at www.waterboards.ca.gov/losangeles/html/meetings/tmdl/tmdl_pollutant_metal.html#LosAngeles.

2.1 Regulatory Background

Section 303(d) of the Federal Water Pollution Control Act (FWPCA) of 1972 and its amendments require that each State “shall identify those waters within its boundaries for which the effluent limitations are not stringent enough to implement any water quality objective applicable to such waters.” The FWPCA also requires states to establish a priority ranking for waters on the 303(d) list of impaired waters and to establish TMDLs for such waters.

The elements of a TMDL are described in 40 CFR 130.2 and 130.7 and Section 303(d) of the CWA, as well as in the U.S. Environmental Protection Agency guidance (USEPA, 2000a). A TMDL is defined as the “sum of the individual waste load allocations for point sources and load allocations for nonpoint sources and natural background” (40 CFR 130.2) such that the capacity of the water body to assimilate pollutant loads (the loading capacity) is not exceeded. A TMDL is also required to account for seasonal variations and include a margin of safety to address uncertainty in the analysis (USEPA, 2000a).

The LAR Metals TMDL was adopted as an amendment to the regional Water Quality Control Plan for the Los Angeles Region (Basin Plan) by the LARWQCB on June 2, 2005 and approved by the USEPA on December 22, 2005. This TMDL became effective January 11, 2006 with the following actions required:

- The TMDL requires responsible agencies to submit a CMP within 15 months after the effective date of the TMDL. Due date: April 11, 2007.
- If conducted, Special Studies Results must be submitted 4 years after the effective date of the TMDL. Due date: January 11, 2010.
- A Draft Implementation Plan must be submitted 4 years after the effective date of the TMDL. Due date: January 11, 2010.
- A Final Implementation Plan must be submitted 4.5 years after the effective date of the TMDL. Due date: July 11, 2010.
- Five years after the effective date of this TMDL the LARWQCB will reconsider it, including certain provisions based on new data, some of which will be collected under this monitoring plan. Projected date: January 11, 2011.
- Responsible jurisdictions and agencies are required to achieve conformance with the Metals TMDL according to the following schedules:

- Six years after the effective date of the TMDL, the MS4 and Caltrans NPDES permittees shall demonstrate that 50% of the total drainage area served by the MS4 is effectively meeting the dry-weather WLAs and 25% of the total drainage area served by the MS4 is effectively meeting the wet-weather WLAs. Projected compliance date: January 11, 2012.
- Fourteen years after the effective date of the TMDL, the MS4 and Caltrans NPDES permittees shall demonstrate that 75% of the total drainage area served by the MS4 is effectively meeting the dry-weather WLAs. Projected compliance date: January 11, 2020.
- Eighteen years after the effective date of the TMDL, the MS4 and Caltrans NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 is effectively meeting the dry-weather WLAs and 50% of the total drainage area served by the MS4 is effectively meeting the wet-weather WLAs. Projected compliance date: January 11, 2024.
- Twenty-two years after the effective date of the TMDL, the MS4 and Caltrans NPDES permittees shall demonstrate that 100% of the total drainage area served by the MS4 is effectively meeting both the dry-weather and wet-weather WLAs. Projected compliance date: January 11, 2028.

This CMP is submitted to fulfill the first of the above requirements.

2.2 TMDL Numeric Targets and Load Allocations

The Los Angeles River dry- and wet-weather numeric water quality targets are based on the numeric standards in the CTR. The TMDL targets are expressed in terms of total recoverable metals to address the potential transformation between total recoverable and dissolved fractions. Separate targets were developed for dry and wet weather, because hardness values and flow conditions in the Los Angeles River and tributaries vary significantly between dry and wet weather.

Dry-weather targets are based on the most limiting of the chronic or acute CTR criteria. For copper and lead, these are the chronic criteria, while for zinc, it is the acute criterion. The dry-weather targets for copper, lead and zinc are dependent on hardness and metals translator factors. The dry-weather target for selenium in Reach 6, and its tributaries, is based on the CTR criterion for total recoverable metals, which is independent of hardness or translator factors.

The City of Los Angeles proposed site-specific copper conversion factors for the areas downstream of the Tillman Plant (Reach 4) and the Glendale Plant (Reach 3) based on a study performed by Larry Walker and Associates (LWA, 2003). CTR default conversion factors for copper are used in the other reaches. CTR default values are used for lead and zinc in all reaches. Application of these default values is applied to the margin of safety for the TMDL.

Wet-weather targets are based on acute criteria developed for cadmium, copper, lead, and zinc as applied to flow and hardness values determined at the Wardlow station in Reach 1. Wet-weather storm conditions are operationally defined when maximum daily flows are equal to or greater than 500 cfs at the LA River Wardlow gauging station and rainfall is observed in the watershed. The 500 cfs value represents the 90th percentile of average daily flow at that station during the period from 1998 to 2000. The dry-weather targets apply to days when the maximum daily flow in the River is less than 500 cfs.

The dry-weather numeric targets and loading capacity and dry- and wet-weather WLAs are tabulated in LARWQCB Basin Plan Amendment No. 2005-006, located in Appendix B.

2.3 TMDL Monitoring Requirements

The LARWQCB identified three monitoring objectives in association with this TMDL. The first is to collect data (e.g., hardness, flow, and background concentrations) to evaluate the uncertainties and assumptions made during development of the TMDL. The second is to collect data to assess compliance with the waste load allocations. The third is to collect data to evaluate potential management scenarios. To achieve these objectives, the LARWQCB suggested utilizing: (1) ambient monitoring, (2) effectiveness monitoring and (3) special studies.

2.3.1 Ambient Monitoring

Per the TMDL language: *“An ambient monitoring program is necessary to assess water quality throughout the Los Angeles River and its tributaries. The MS4 and Caltrans NPDES permittees assigned waste load allocations in each jurisdictional group are jointly responsible for implementing the ambient monitoring program. The responsible agencies shall sample for total recoverable metals, dissolved metals, and hardness once per month at each ambient monitoring location until at least year five when the TMDL is reconsidered.”*

2.3.2 Effectiveness Monitoring

Per the TMDL language: *“The MS4 and Caltrans stormwater NPDES permittees in each jurisdictional group are jointly responsible for assessing progress in reducing pollutant loads to achieve the TMDL. Each jurisdictional group is required to submit for approval by the Executive Officer a coordinated monitoring plan that will demonstrate the effectiveness of the phased implementation schedule for this TMDL which requires that the waste load allocations be met in prescribed percentages of each sub watershed over a 22-year period. The monitoring locations specified for the ambient monitoring program may be used as effectiveness monitoring locations.”*

The stormwater NPDES permittees will be found to be effectively meeting the dry-weather waste load allocations if the in-stream pollutant concentration or load at the first downstream effectiveness monitoring location is equal to or less than the corresponding concentration- or load-based waste load allocation. Alternatively, effectiveness of the TMDL may be assessed at the storm drain outlet based on the numeric target for the receiving water. For storm drains that discharge to other storm drains, effectiveness will be based on the waste load allocation for the ultimate receiving water for that storm drain system.

The stormwater NPDES permittees will be found to be effectively meeting wet-weather waste load allocations if the loading at the downstream monitoring location is equal to or less than the daily storm volume multiplied by the wet-weather numeric targets as defined in the table below. For practical purposes, this is when the EMC is less than or equal to the numeric target.”

2.3.3 Special Studies

Additional monitoring and special studies are being proposed to evaluate uncertainties and the assumptions made in development of this TMDL; however, the special studies are voluntarily funded and not part of this mandatory CMP proposal.

2.3.4 Coordinated Monitoring Plan Development

The members of the LAR Metals TMDL TC developed this monitoring plan. The City of Los Angeles and the Los Angeles County Department of Public Works co-chair the TC, with representatives from the Jurisdictional (Reach) Areas including the cities of Burbank, Downey, Glendale, Hidden Hills, Irwindale, Long Beach, Pasadena, Signal Hill, and Caltrans comprising the other members. Based on a draft of the CMP and expected monitoring costs, the TMDL identified responsible municipalities were requested to respond in writing to Los Angeles County to confirm participation in the LAR Metals TMDL CMP and subsequent ambient monitoring effort. The TC is pleased to report a nearly unanimous affirmation of commitment as indicated in Appendix K, on which basis a funding agreement will be developed.

3. MONITORING SITES

3.1 Los Angeles River Watershed Setting

As defined by the LARWQCB, the Los Angeles River Watershed drains an area of 834 square miles. The Los Angeles River headwaters in the Santa Monica, Santa Susana, and San Gabriel Mountains, including the Angeles National Forest, comprises approximately 200 square miles (24%) of the watershed. At this time, the LARWQCB has excluded these areas from any TMDL requirements. The more urban uses are found in the lower portions of the watershed, where approximately 36% of the land use can be categorized as residential, 20% open or natural space, 10% as industrial, 8% as commercial, and 3% as agriculture, water and other.

The Los Angeles River flows for 55 miles from the Santa Monica Mountains at the western end of the San Fernando Valley to Queensway Bay located between the Port of Long Beach and the City of Long Beach. Due to shifting drainage flow paths, the natural hydrology of the Los Angeles River Watershed has been altered by channelization and the construction of dams and flood control reservoirs. The Los Angeles River and many of its tributaries are lined with concrete for most or all of their lengths. Soft-bottomed segments of the Los Angeles River only occur where groundwater upwelling prevented armoring of the river bottom.

Los Angeles River Watershed is divided by the LARWQCB into six jurisdictional groups based on river reach; refer to page 21, Table 7-13.3 of the Basin Plan Amendment in Appendix B for a list of the responsible agencies in each jurisdiction.

Several monitoring efforts have taken place within the Los Angeles River Watershed. Beginning in 2002, the City of Los Angeles, Department of Public Works, Bureau of Sanitation, Watershed Protection Division, under its Status and Trends Monitoring Program, began monthly monitoring at eight (8) locations along the main channel of Los Angeles River for bacteria, metals, and other pollutants. In 2005 this Status and Trends Program was extended to include ten (10) tributary monitoring locations. The County of Los Angeles, as part of the Los Angeles County Municipal Stormwater Permit Core Monitoring Program, also conducts sampling within the Los Angeles River Watershed. The County's Core Monitoring Program is comprised of one permanent mass emission station within the main channel. To assess wet-weather impairments, the County has been sampling approximately three to five storms per year at the Wardlow gauging station since 1996. The County samples hardness and metals (both dissolved and total recoverable metals) from composite stormwater samples.

3.2 Monitoring Locations

The monitoring sites for the LAR Metals TMDL CMP have been selected by the TC. As part of the evaluation process, the TC considered the current 303(d) listed reaches, future TMDLs, available data including POTW monitoring locations, and conducted site

investigations to determine potential ambient and effectiveness monitoring locations. The final list of monitoring sites was selected based on professional judgment, the requirements of the TMDL and the monitoring tiers presented below; these sites are characterized in Appendix C.

3.2.1 Wet- and Dry-Weather Water Quality Monitoring

Monitoring to comply with the LAR Metals TMDL establishes dry- and wet-weather water quality monitoring locations within the Los Angeles River watershed for two distinct purposes: 1) to characterize ambient water quality and 2) to measure attainment of WLAs specified in the effectiveness monitoring portion of the TMDL. Effectiveness monitoring may utilize many of the same dry- and wet-weather water quality monitoring locations, within the Los Angeles River watershed, as are used to characterize ambient water quality.

Water quality effectiveness monitoring will be accomplished through a three-tiered approach to meet the TMDL requirements. This monitoring approach provides the responsible agencies with a predetermined set of locations to investigate sources of possible exceedences that may occur at the CMP locations.

Three Tier Monitoring Approach:

1. Tier I – Main River Sampling – Nine (9) sample points are located in the main channel/stem of the river and large portions of discharge area contribute to the potential runoff at these points. (Note that 8 were required by the TMDL.)
2. Tier II – Tributary Sampling – These sampling points are upstream of the Tier I locations, but at the most downstream end of each tributary. They should reflect the contribution of each tributary flow to the main stem of the river.
3. Tier III – Investigatory Sampling – These intra-jurisdictional monitoring locations will be determined as appropriate during the effectiveness phase.

Most of the nine (9) Tier I ambient monitoring sampling locations, each representing major portions of the total drainage area, were identified in the LAR Metals TMDL and may later be used for effectiveness monitoring. Once effectiveness monitoring is required by the TMDL, the Tier II Activation and Deactivation Criteria listed below will be applied to the data from the Tier I locations to determine when monitoring at the upstream Tier II locations would begin and end; in order to narrow the search for the source of the exceedence(s). The seven (7) Tier II locations were selected by further subdividing the watershed into smaller tributary areas that each represent approximately 3 – 26 % of the entire watershed. The Tujunga Wash Tributary area is the largest Tier II location draining 26% of the watershed, but 74% of the land use is in the U.S Forest and less than 7% is the responsibility of the MS4 permittees. Similarly, almost 20% of the Rio Hondo tributary area is in the National Forest.

Tier II Activation Criteria:

- There are 3 consecutive exceedences of WLA(s) at a Tier I monitoring site

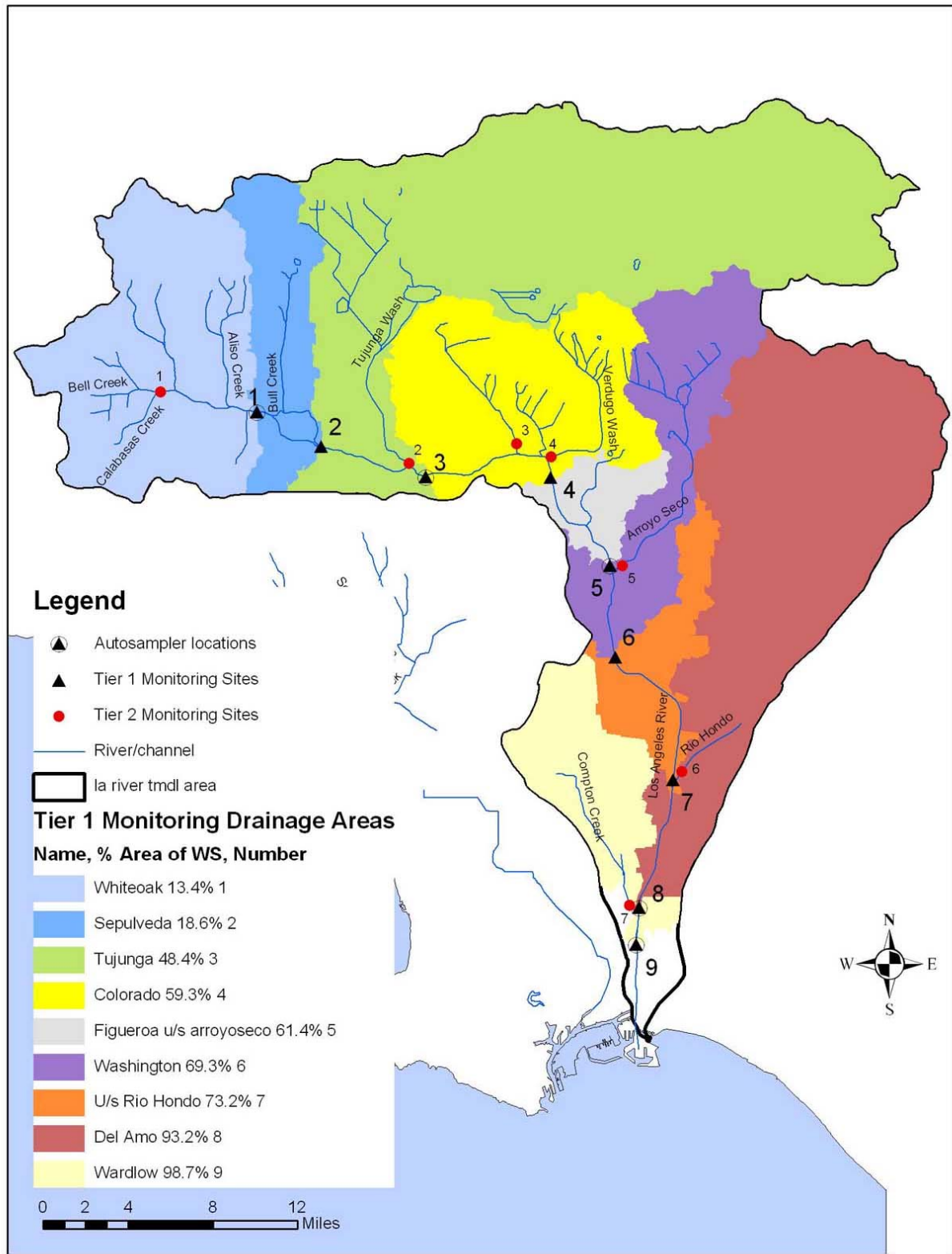
Tier II Deactivation Criteria:

- Data from 3 consecutive Tier II monitoring events is less than the WLA(s)

Tier II monitoring will only be conducted at the Tier II sites that are immediately upstream of a Tier I site where the WLA exceedences occurred. If a Tier II location is consistently not meeting the water quality standards, Tier III monitoring will initiate with a source tracking investigation to attempt to identify the source(s) causing the exceedences, so that the responsible agencies can take the necessary corrective measures to resolve the problem. Tier II and Tier III monitoring will normally only target the constituent(s) that exceeded the WLA at the Tier I site.


Approximate locations of the Tier I and II sampling sites are shown in the following figure. The drainage areas to these locations are outlined in Appendix C.


Tier I and II Monitoring Locations





Tier I Locations


In accordance with the TMDL requirements, the responsible agencies propose to conduct monthly ambient/effectiveness sampling at the following nine (9) Tier I locations (LAR-1 through LAR-9), each of which is accompanied by a brief description. Additional details, including drainage maps and locations, of these sites are available in Appendix C.


Site Id: LAR1 – 1	Status: Existing	Location: Main Channel
Historical Site Id: White Oak	Subwatershed: N/A	Sampling Details: Autosampler
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at White Oak Avenue on the main channel. This site receives flow from 13.4% of the total drainage area and is located in Jurisdiction/Reach 6.		


Site Id: LAR1 – 2	Status: Existing	Location: Main Channel
Historical Site Id: Sepulveda	Subwatershed: N/A	Sampling Details: Grab
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at Sepulveda Blvd. on the main channel. This site receives flow from 18.6% of the total drainage area and is located in Jurisdiction/Reach 5.		


Site Id: LAR1 – 3	Status: Existing	Location: Main Channel
Historical Site Id: Tujunga	Subwatershed: N/A	Sampling Details: Autosampler
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at Tujunga Blvd. on the main channel. This site receives flow from 48.5% of the total drainage area and is located in Jurisdiction/Reach 4.		


Site Id: LAR1 – 4	Status: Existing	Location: Main Channel
Historical Site Id: Colorado	Subwatershed: N/A	Sampling Details: Grab
Comments: The sampling site is currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. It is located in the main channel downstream from the Colorado Blvd. Bridge. This site receives flow from 59.5% of the total drainage area and is located in Jurisdiction/Reach 3.		

Site Id: LAR1 – 5	Status: Existing	Location: Main Channel
Historical Site Id: Figueroa	Subwatershed: N/A	Sampling Details: Autosampler
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located upstream of the Arroyo Seco confluence at Figueroa St./Riverside Dr. bridge on the main channel. This site receives flow from 61.4% of the total drainage area and is located at the bottom of Jurisdiction/Reach 3.		

Site Id: LAR1 – 6	Status: Existing	Location: Main Channel
Historical Site Id: Washington	Subwatershed: N/A	Sampling Details: Grab
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The site is located at Washington Blvd. on the main channel. This site receives flow from 69.3% of the total drainage area and is located in Jurisdiction/Reach 2.		

Site Id: LAR1 – 7	Status: New	Location: Main Channel
Historical Site Id: 710 Freeway	Subwatershed: N/A	Sampling Details: Grab
Comments: This is a new sampling site located between the 710 freeway bridge on the north and Imperial Highway bridge on the south in the main channel upstream of the Rio Hondo confluence. This site receives flow from 73.2% of the total drainage area and is located in Jurisdiction/Reach 2.		


Site Id: LAR1 – 8	Status: New	Location: Main Channel
Historical Site Id: Del Amo	Subwatershed: N/A	Sampling Details: Autosampler
Comments: This is a new sampling site located in Long Beach at Del Amo Blvd. in the main channel upstream of the Compton Creek confluence. This site receives flow from 93.2% of the total drainage area and is located at the bottom of Jurisdiction/Reach 2.		


Site Id: LAR1 – 9	Status: Existing	Location: Main Channel
Historical Site Id: Wardlow (S10)	Subwatershed: N/A	Sampling Details: Autosampler
Comments: This is an existing Los Angeles County mass emission sampling site located in Long Beach south of Wardlow Road and north of Willow St. in the main channel. This is the location of an existing Los Angeles County gauging station identified as F319-R. This site receives flow from 98.7% of the total drainage area and is located in Jurisdiction/Reach 1		


Tier II Locations


Tier II monitoring locations consist of a total of seven (7) sites where additional samples can be taken if data from Tier I locations are found to consistently exceed the effectiveness program WLAs. Several of these Tier II locations were used in LA County's Core Monitoring Program under the LA County Municipal Stormwater Permit. A description of each location follows:


Approximate locations of these sites are shown in Table 2 in Appendix C.


Site Id: LAR2 – 1	Status: New	Location: Tributary
Historical Site Id: Bell & Calabasas	Subwatershed: Bell Creek and Calabasas Creek	
Comments: This is a new sampling site, located just below the confluence of Bell Creek and Calabasas Creek at Canoga Ave. This site receives flow from 4.8% of the total drainage area and is located in Jurisdiction/Reach 6.		


Site Id: LAR2 – 2	Status: Existing	Location: Tributary
Historical Site Id: Tujunga Wash @ Moorpark	Subwatershed: Tujunga Wash	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. The location is in the Tujunga Wash channel at Moorpark St. This sampling site receives flow from 26.2% of the total drainage area and is located in Jurisdiction/Reach 4.		

Site Id: LAR2 – 3	Status: Existing	Location: Tributary
Historical Site Id: TS03	Subwatershed: Burbank Western Channel	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. It is also currently monitored by Los Angeles County's Core Monitoring Program under the LA County Municipal Stormwater Permit and identified as the Burbank Western System Monitoring Station (TS03). This sampling site (Burbank Western Channel at Riverside Dr.) receives flow from 3.0% of the total drainage area and is located in Jurisdiction/Reach 3.		

Site Id: LAR2 – 4	Status: Existing	Location: Tributary
Historical Site Id: Verdugo @ Concord	Subwatershed: Verdugo Wash	
Comments: This is a new sampling site located on the Verdugo Wash at San Fernando Rd. This site receives flow from 3.6% of the total drainage area and is located in Jurisdiction/Reach 3.		

Site Id: LAR2 – 5	Status: Existing	Location: Tributary
Historical Site Id: Arroyo Seco @ San Fernando Rd.	Subwatershed: Arroyo Seco	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. This site receives flow from 5.6% of the total drainage area and is located in Jurisdiction/Reach 2.		

Site Id: LAR2 – 6	Status: Existing	Location: Tributary
Historical Site Id: Rio Hondo @ Garfield Ave.	Subwatershed: Rio Hondo	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. This site receives flow from 16.7% of the total drainage area and is located in Jurisdiction/Reach 2.		

Site Id: LAR2 – 7	Status: Existing	Location: Tributary
Historical Site Id: Compton Creek @ Del Amo Blvd.	Subwatershed: Compton Creek	
Comments: This is an existing sampling site currently monitored by the City of Los Angeles as part of its Status and Trends Monitoring Program. This site receives flow from 5.0% of the total drainage area and is located in Jurisdiction/Reach 1.		

4. Sampling Parameters, Schedule, and Reporting

4.1 Introduction

This section of the CMP provides the scope and methods to be used in collecting, transporting, sampling, and reporting for the metals and related water quality parameters required by the LAR Metals TMDL. This section also characterizes the data analysis and reporting considerations as related to the ambient and effectiveness monitoring requirements. Unless otherwise noted, this section proposes the utilization of state and federally approved methods, materials, and analysis requirements. Many of the supporting documents, included as appendices in the CMP, are finalized CLABOS, Environmental Monitoring Division, Hyperion Treatment Plant Laboratory Protocols (SOP). Pending Board approval of the CMP and completion of interagency contractual agreements, these documents were chosen as being most representative of those that will be provided in the final CMP and used during the ambient monitoring effort.

4.2 Sampling Parameters

The only TMDL identified selenium impairment is within reach 6 and the most likely source is natural marine derived soils which are prevalent in this jurisdictional area. Samples taken from reach 6 may be analyzed using method 200.8, which the City of Los Angeles has found to result in comparable selenium detection limits of 2 ug/L. The method is sufficiently below the TMDL required load allocation based concentration limits.

On November 30, 2006, the USEPA adopted the final California 2006 303(d) list. On this list, cadmium has been de-listed from the Burbank Western Channel and Reach 1 of the Los Angeles River. Therefore, the Los Angeles River is no longer impaired for cadmium and we propose that no cadmium analysis be conducted.

The metals to be monitored as a result of the LAR Metals TMDL include the following:

- Copper (Cu)
- Lead (Pb)
- Selenium (Se)(Reach 6, dry-weather only)
- Zinc (Zn)

In addition to the above parameters, the jurisdictions will also monitor for Hardness as required by the LAR Metals TMDL. Table 4.1 below outlines the constituent parameters to be monitored, testing method, detection level, and related information.

Table 4.1 - Sampling and Analytical Requirements for Metals & Other Parameters

Analysis	Method ^[1,5]	Minimum Level ^[2]	Required Sample Volume (min.) ^[3]	Preservative	Sample Bottles ^[4]	Holding Time	Laboratory
Hardness	SM 2340B or C		100 mL	HNO ₃ or H ₂ SO ₄ to pH <2	Plastic (polyethylene or equivalent)	6 months	City of Los Angeles
Copper, total	EPA 200.7 /SM 3120A	10 ug/L	1000 mL	If stored add 0.5 mL 1+1 HCl or HNO ₃ to pH <2	Plastic (polyethylene or equivalent)	6 months	City of Los Angeles
Lead, total	EPA 200.7/SM 3120A	5 ug/l	1000 mL			6 months	City of Los Angeles
Selenium, total	EPA 200.8/(SM 3125A)	2 ug/L	1000 mL			6 months	City of Los Angeles
Zinc, total	EPA 200.7/SM 3120A	20 ug/L	1000 mL			6 months	City of Los Angeles

Notes to Table ##:

[1] US EPA Methods as approved in 40 CFR Part 136, and 22 CCR § 64811. (c) (2006). Procedures with SM refer to Standard Methods for the Examination of Water and Wastewater, 18th, 19th, or 20th Edition (APHA, AWWVA, WEF, 1999) as referred to and approved in 40 CFR Part 136.

[2] Minimum Levels were obtained from the City of Los Angeles Laboratory SOP found in Appendix G. The ML represents the lowest concentration at which an analyte can be measured with a known level of confidence. The Minimum Level (ML) is equivalent to the lowest calibration standard analyzed by the specific analytical procedure.

[3] Obtained from SM, Table 1060:I Summary of Special Sampling and Handling Requirements.

[4] The Sample Bottle column indicates the bottle and preservative used in the field, see note 3 above.

[5] USEPA Method 200.7 as approved in 40 CFR Part 136 and as reviewed from http://www.epa.gov/safewater/methods/inch_tbl.html. Last visited and verified as of December 29, 2006

4.3 Sampling Schedule

Through this CMP, the responsible agencies have provided an effective and reasonable sampling schedule as required by the TMDL. Table 4.2 below outlines the dry and wet weather sampling and monitoring schedule covered by this CMP. As the water quality objectives of this TMDL are achieved and impairments eliminated, analyses for constituents that are delisted would cease and the monitoring resources reallocated to controlling the remaining impairments.

Table 4.2 Water Quality Monitoring Frequency

Monitoring Event	Analyses	Monitoring Frequency
Dry-Weather	Copper Lead Selenium Zinc Hardness	Monthly, unless pre-empted by collection of a wet-weather sample.
Wet-Weather	Copper Lead Zinc Hardness	Per wet-weather event, but not to exceed more than 1 sample event per month with a minimum of 72 hours between storm events.

4.4 Collection and Transportation

The CMP will employ generally accepted methods for sample collection and transportation. As indicated in Table 4.2 above, sample collection is categorized into dry and wet weather monitoring events. During dry weather events samples will be collected using the grab technique, and during wet-weather events automated samplers will be used, where available, to collect composite samples. Dry and wet weather sample collections will be taken at the monitoring stations identified in Section 3.0.

4.4.1 Dry-Weather Sample Collections

Dry weather grab samples are scheduled to be collected on a monthly basis, unless a qualifying wet-weather sample is collected first. Samples will be collected from the approved sites identified in Section 3.0. Samples will be collected in approved containers and using standard methods. Examples of specific methods of collection and preservation, where applicable, are more fully described in the Appendix D.

4.4.2 Wet-Weather Sample Collections

Five (5) of the nine (9) Tier I locations described in Section 3.0 will have autosamplers installed for wet-weather sample collections and flow monitoring.

See Appendix C for a complete map of these locations. Flow-weighted composite samples will be collected at these locations to obtain the representative sample for each storm event. A flow-weighted composite sample is obtained by mixing a series of discrete samples (aliquots) of specific volume, collected at specific runoff volume intervals over the duration of the storm event. An autosampler will be programmed to start automatically when the water level in the channel or storm drain exceeded a certain height such that the corresponding flow rate exceeded a pre-determined wet weather flow rate at the sampling location. The automated sampler will be programmed with the intent of capturing the major portion of a runoff event. Appendix D describes in more details an example of the wet weather sampling procedure using autosamplers.

Autosamplers will only be considered for installation at Tier II locations as indicated by the results from Tier I monitoring (i.e., there may be some Tier II locations where the installation of an autosampler is unnecessary). Some Tier II stations may require expensive infrastructure design and construction to accommodate composite samplers. In these cases, if safety considerations allow, grab sampling will be conducted during wet weather until auto-samplers are operational and flow calibrated.

4.4.3 Employee (Sample Collector) Safety

In an effort to improve employee safety, health awareness, and prevent occupational-related injury and illness, participating laboratories must have a safety program that satisfies applicable federal, state, and local regulations. It is the policy of the participating agencies to have a safe working environment for all of their employees and that all field and laboratory work be performed in a manner that provides the maximum level of safety for the protection of every employee. See Appendix E for detailed safety protocols for field collection activities.

4.4.4 Specific Procedures

Following the collection and preservation, each sample will be marked with an identifying name or sample number and placed on ice if so required. All samples that are collected will be documented with an appropriate chain-of-custody (COC) form that will describe the sample number, time of day, ambient local weather conditions, collector's name, date, time, and other related information. This custody form will be kept with the sample until delivery to the appropriate laboratory for testing. Where there may be multiple samples collected during one trip/day, one or more custody forms can or may be used. The sample collection staff will clearly indicate the specific sample by alphanumerical designation or other indicator of sample containers. See Appendix F for a sample COC currently being used by City of Los Angeles-Environmental Monitoring Division (EMD). All samples collected while in the field, during both wet and dry collection periods will be transported to the designated laboratory as soon after collection as possible and will comply with state and federal transportation requirements for the applicable parameters.

Upon delivery to the appropriate lab, the collection staff will require the lab to sign for the samples, indicating name of person receiving the sample, time, date, and other comments on the status or condition of the samples. Following delivery, the sample collection staff, will remove or make a copy of the custody form for retention purposes. All custody form copies will be maintained for the prescribed period. These forms may also be digitized for record maintenance purposes.

4.5 Analytical Methodology

This CMP will utilize the Inductively Coupled Plasma—Atomic Emission Spectrometric Method (“ICP-AES” or “ICP”) for most water quality metal analyses. This method is approved for ambient water quality monitoring by the U.S. and California EPAs, pursuant to 40 CFR Part 136 and 22 CCR §64801 *et. seq.* ¹ USEPA ICP Method 200.7 has the ability to detect constituent concentrations below that of the identified TMDL compliance requirements. Typical Standard Operating Procedures (SOPs) for the ICP procedure are attached as Appendix G. Due to the reach 6 specific selenium requirement, methods 200.8 or 3125A will be used.

The TC has determined that the Inductively Coupled Plasma—Mass Spectrometric Method, or “ICP-MS” method 200.8, is only necessary for reach 6 Selenium sample analysis because: 1) proposed TMDL limits are fully recognized using the ICP-AES method; and 2) the ICP-MS method doubles the cost of sampling events. The agencies may pursue a special study to verify the translators used for this TMDL and may sample for dissolved metal levels at that time.

Table 4.3 Water Quality Monitoring

TMDL	Analyses	Analytical Methodology*
LA River Metals	Hardness	Method 2340B or C of Standard Methods, 18-20 th Edition
	Copper, Lead, & Zinc	EPA 200.7

* Detailed Standard Operating Procedures for these methods can be found in Appendix G

All laboratories performing analyses for TMDL monitoring shall maintain Environmental Laboratory Accreditation Program certification (ELAP) as administered by the California Department of Health Services for all testing methods. Additionally, all laboratories shall submit detailed SOPs for review by LARWQCB staff upon request. Appendix G provides examples of SOPs developed by EMD. The lab shall ensure that each analytical method used for the TMDL monitoring program shall be an approved EPA or Standard Methods for the Examination of Water and Wastewater, 18th-20th edition (APHA 1992-98)

¹ As approved in 40 CFR § 136.1-5 (2006) and 22 CCR § 64811. (c) (2006).

method. Laboratories, following LARWQCB approval, may use other approved and accepted analytical methods for TMDL monitoring.

4.6 Quality Assurance/Quality Control

If multiple laboratories are used, each will participate in an inter-laboratory calibration program to ensure consistency of results. All laboratories must employ a program that assesses and documents quality assurance for the laboratory facility, staff, instrumentation and equipment, materials and methods, reagents, and data validation. These QA/QC measures may be included in the submitted SOPs or defined in a separate QA/QC document such as Appendix H. The quality assurance procedures shall be in accordance with Standard Methods for the Examination of Water and Wastewater, 18-20th Editions (APHA 1992-98). All participating laboratories must maintain ELAP certification, and provide QA/QC documentation as required by the LARWQCB.

4.7 Reporting Protocols

All data collected will be archived within a database. Copies of the annual reports will be distributed to the responsible agencies prior to submittal to the LARWQCB for review and approval. The final summary reports will be submitted to the LARWQCB on an annual basis along with compliance summary tables. See Appendix I for examples of data acquisition, reduction, validation, and reporting SOPs.

APPENDIX A

Development History of Los Angeles River Metals TMDLs

States must develop water quality management plans to implement the TMDL (40 CFR 130.6). The USEPA has oversight authority for the 303(d) program and is required to review and either approve or disapprove the TMDLs submitted by states. In California, the SWRCB and the nine RWQCBs are responsible for preparing lists of impaired water bodies under the 303(d) program and for preparing TMDLs, both subject to USEPA approval. If USEPA disapproves a TMDL submitted by a state, USEPA is required to establish a TMDL for that water body. The RWQCBs also hold regulatory authority for many of the instruments used to implement the TMDLs, such as the National Pollutant Discharge Elimination System (NPDES) permits and state-specified Waste Discharge Requirements (WDRs).

The LARWQCB identified over 700 water body-pollutant combinations in the Los Angeles Region requiring TMDLs (LARWQCB, 1996, 1998a). These are referred to as “listed” or “303(d) listed” water bodies or water body segments. In December 1997, the Natural Resources Defense Council (NRDC), acting as legal representative for Heal the Bay, Inc., and Santa Monica BayKeeper, Inc., filed a Notice of Intent to sue the USEPA over failure of the LARWQCB to adequately implement the 303(d)/TMDL Program. In December 1998, NRDC and BayKeeper entered into a Federal Consent Decree with the USEPA. The Consent Decree combined the more than 700 water body-pollutant combinations into 92 TMDL analytical units, which are water quality limited segments and associated pollutants for which TMDLs must be developed. A schedule for development of TMDLs in the Los Angeles Region was established in this consent decree.

This TMDL addresses Analytical Unit (AU) #13 of the Consent Decree, which consists of segments of the Los Angeles River and tributaries with impairments by metals (cadmium, copper, lead, selenium, and zinc). The Consent Decree schedule requires that this TMDL be completed by March 22, 2004. If the LARWQCB fails to develop the TMDL, USEPA must promulgate the TMDL by March 22, 2005. USEPA and the consent decree plaintiffs recently agreed to extend the completion deadline to December 22, 2005, in order to enable the State to complete its adoption process and USEPA to approve the State-adopted TMDLs for this water body. The 2002 303(d) listings approved in 2003 are not required to be addressed per the Consent Decree; however, where appropriate, this TMDL addresses those listings as well. These TMDLs have not been specifically scheduled in the Consent Decree, but are required to be completed by 2012.

The proposed TMDL for metals has been adopted as an amendment to the Regional Board's *Water Quality Control Plan for the Los Angeles Region* (Basin Plan). The Secretary of Resources has certified the basin planning process as

exempt from certain requirements of the California Environmental Quality Act (CEQA), including preparation of an initial study, negative declaration, and environmental impact report (California Code of Regulations, Title 14, Section 15251(g)). The Basin Plan amendment and supporting documents, including this staff report and the CEQA checklist are considered substitute documents to an initial study, negative declaration, or environmental impact report. LARWQCB staff held a CEQA Scoping meeting on April 23, 2004 in order to receive stakeholder input on the scope and content of the TMDL documents. LARWQCB Staff presented an overview of reasonably foreseeable means of compliance with the TMDL in order to facilitate the scoping discussion and to identify possible impacts of the TMDL implementation. The TMDL was approved by the USEPA and became effective on January 11, 2006.

APPENDIX B

Basin Plan

The Los Angeles Regional Water Quality Control Board's (LARWQCB) Basin Plan is designed to preserve and enhance water quality and protect the beneficial uses of all regional waters. Specifically, the Basin Plan (i) designates beneficial uses for surface and ground waters, (ii) sets narrative and numerical objectives that must be attained or maintained to protect the designated beneficial uses and conform to the state's antidegradation policy, and (iii) describes implementation programs to protect all waters in the Region. In addition, the Basin Plan incorporates (by reference) all applicable State and RWQCB plans and policies and other pertinent water quality policies and regulations. Those of other agencies are referenced in appropriate sections throughout the Basin Plan.

The Basin Plan is a resource for the LARWQCB and others who use water and/or discharge wastewater in the Los Angeles Region. Other agencies and organizations involved in environmental permitting and resource management activities also use the Basin Plan. Finally the Basin Plan provides valuable information to the public about local water quality issues.

The Basin Plan is reviewed and updated as necessary. Following adoption by the RWQCB, the Basin Plan and subsequent amendments are subject to approval by the SWRCB, the State Office of Administrative Law (OAL), and the USEPA.

The Basin Plan is attached below and can also be downloaded from the LARWQCB's website:

http://www.swrcb.ca.gov/rwqcb4/html/meetings/tmdl/Basin_plan/basin_plan.html

**Amendment to the Water Quality Control Plan – Los Angeles Region to incorporate the
Los Angeles River and Tributaries Metals TMDL**

Adopted by the California Regional Water Quality Control Board, Los Angeles Region on June 2, 2005.

Amendments:

Table of Contents

Add:

Chapter 7. Total Maximum Daily Loads (TMDLs)
Summaries 7-13 Los Angeles River and
Tributaries Metals TMDL

List of Figures, Tables and Inserts

Add:

Chapter 7. Total Maximum Daily Loads (TMDLs)
Tables
7-13 Los Angeles River and Tributaries Metals TMDL

Table 7-13.1 Los Angeles River and Tributaries Metals TMDL: Elements Table 7-13.2
Los Angeles River and Tributaries Metals TMDL: Implementation Schedule Table 7-
13.3 Los Angeles River and Tributaries Metals TMDL: Jurisdictional Groups

**Chapter 7. Total Maximum Daily Loads (TMDLs) Summaries, Section 7-13 (Los Angeles
River and Tributaries Metals TMDL)**

Add:

This TMDL was adopted by

The Regional Water Quality Control Board on June 2, 2005.

This TMDL was approved by:

The State Water Resources Control Board on [Insert Date].
The Office of Administrative Law on [Insert Date].
The U.S. Environmental Protection Agency on [Insert Date].

The following table includes the key elements of this TMDL.

Table 7-13.1 Los Angeles River and Tributaries Metals TMDL: Elements

Element	Key Findings and Regulatory Provisions
<i>Problem Statement</i>	<p>Segments of the Los Angeles River and its tributaries are on the Clean Water Act section 303(d) list of impaired waterbodies for copper, cadmium, lead, zinc, aluminum and selenium. The metals subject to this TMDL are toxic pollutants, and the existing water quality objectives for the metals reflect national policy that the discharge of toxic pollutants in toxic amounts be prohibited. When one of the metals subject to this TMDL is present at levels exceeding the existing numeric objectives, then the receiving water is toxic. The beneficial uses impaired by metals in the Los Angeles River and its tributaries are those associated with aquatic life and water supply, including wildlife habitat, rare, threatened or endangered species, warm freshwater habitat, wetlands, and groundwater recharge. TMDLs are developed for reaches on the 303(d) list and for reaches where recent data indicate additional impairments. Addressing the impairing metals throughout the Los Angeles River watershed will ensure that the metals do not contribute to an impairment elsewhere in the watershed. Metals allocations are therefore developed for upstream reaches and tributaries that drain to impaired reaches. These TMDLs address wet- and dry-weather discharges of copper, lead, zinc and selenium and wet-weather discharges of cadmium. Impairments related to cadmium only occur during wet weather. Impairments related to selenium are confined to Reach 6 and its tributaries. Dry-weather impairments related to zinc only occur in Rio Hondo Reach 1. The aluminum listing was based on water quality objectives set to support the municipal water supply beneficial use (MUN). MUN is a conditional use in the Los Angeles River watershed. The United States Environmental Protection Agency (USEPA) has determined that TMDLs are not required for impairments of conditional uses.</p>

<p><i>Numeric Target</i> <i>(Interpretation of the numeric water quality objective, used to calculate the waste load allocations)</i></p>	<p>Numeric water quality targets are based on the numeric water quality criteria established by the California Toxics Rule (CTR). The targets are expressed in terms of total recoverable metals. There are separate targets for dry and wet weather because hardness values and flow conditions in the Los Angeles River and tributaries vary between dry and wet weather. The dry-weather targets apply to days when the maximum daily flow in the River is less than 500 cfs. The wet-weather targets apply to days when the maximum daily flow in the River is equal to or greater than 500 cfs.</p> <p>The dry-weather targets for copper and lead are based on chronic CTR criteria. The dry-weather targets for zinc are based on acute CTR criteria. Copper, lead and zinc targets are dependent on hardness to adjust for site specific conditions and conversion factors to convert between dissolved and total recoverable metals. Copper and lead targets are based on 50th percentile hardness values. Zinc targets are based on 10th percentile hardness values. Site-specific copper conversion factors are applied immediately downstream of the Tillman and LA-Glendale</p>
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Element	Key Findings and Regulatory Provisions				
	water reclamation plants (WRP). CTR default conversion factors are used for copper, lead, and zinc in all other cases. The dry-weather target for selenium is independent of hardness or conversion factors.				
	Dry-weather conversion factors:				
		Default	Below Tillman WRP	Below LA-Glendale WRP	
	Copper	0.96		0.74	0.80
	Lead	0.79			
	Zinc	0.61			
	Dry-weather numeric targets (µg total recoverable metals/L)				
		Cu	Pb	Zn	Se
	Reach 5, 6 and Bell Creek	30	19		5
	Reach 4	26	10		
	Reach 3 above LA-Glendale WRP and Verdugo	23	12		
	Reach 3 below LA-Glendale WRP	26	12		
	Burbank Western Channel (above WRP)	26	14		
	Burbank Western Channel (below WRP)	19	9.1		
	Reach 2 and Arroyo Seco	22	11		
	Reach 1	23	12		
	Compton Creek	19	8.9		
	Rio Hondo Reach 1	13	5.0	131	
	Monrovia Canyon		8.2		
	The wet-weather targets for cadmium, copper, lead and zinc are based on acute CTR criteria and the 50th percentile hardness values for storm water collected at the Wardlow gage station. Conversion factors for copper, lead and zinc are based on a regression of dissolved metals values to total recoverable metals values collected at Wardlow. The CTR default conversion factor is applied to cadmium. The wet-weather target for selenium is independent of hardness or conversion factors. Wet-weather conversion factors:				
	Cadmium	0.94			
	Copper	0.65			
	Lead	0.82			
	Zinc	0.61			
	Wet-weather numeric targets (µg total recoverable metals/L)				
		Cd	Cu	Pb	Zn
		3.1	17	62	159
					5

Element	Key Findings and Regulatory Provisions
<i>Source Analysis</i>	<p>There are significant differences in the sources of metals loadings during dry weather and wet weather. During dry weather, most of the metals loadings are in the dissolved form. The three major publicly owned treatment works (POTWs) that discharge to the river (Tillman WRP, LA-Glendale WRP, and Burbank WRP) constitute the majority of the flow and metals loadings during dry weather. The storm drains also contribute a large percentage of the loadings during dry weather because although their flows are typically low, concentrations of metals in urban runoff may be quite high. The remaining portion of the dry weather flow and metals loadings represents a combination of tributary flows, groundwater discharge, and flows from other permitted NPDES discharges within the watershed.</p> <p>During wet weather, most of the metals loadings are in the particulate form and are associated with wet-weather storm water flow. On an annual basis, storm water contributes about 40% of the cadmium loading, 80% of the copper loading, 95% of the lead loading and 90% of the zinc loading. This storm water flow is permitted through two municipal separate storm sewer system (MS4) permits, a separate Caltrans MS4 permit, a general construction storm water permit and a general industrial storm water permit.</p> <p>Nonpoint sources of metals may include tributaries that drain the open space areas of the watershed. Direct atmospheric deposition of metals on the river is also a small source. Indirect atmospheric deposition on the land surface that is washed off during storms is a larger source, which is accounted for in the estimates of storm water loadings.</p> <p>The sources of selenium appear to be related to natural levels of selenium in soils in the upper watershed. Separate studies are underway to evaluate whether selenium levels represent a “natural condition” for this watershed.</p>
<i>Loading Capacity</i>	<p>Dry Weather Dry-weather TMDLs are developed for the following pollutant waterbody combinations (allocations are developed for upstream reaches and tributaries to meet TMDLs in downstream reaches):</p> <ul style="list-style-type: none"> • Copper for the Los Angeles River Reaches 1, 2, 3, 4, and 5, Burbank Channel, Compton Creek, Tujunga Wash, Rio Hondo Reach 1. • Lead for the Los Angeles River Reaches 1, 2, 3, 4, and 5, Burbank Channel, Rio Hondo Reach 1, Compton Creek, Monrovia Canyon Creek. • Zinc for Rio Hondo Reach 1. • Selenium for Reach 6, Aliso Creek, Dry Canyon Creek, McCoy Canyon Creek. <p>For dry weather, loading capacities are equal to reach-specific numeric targets multiplied by reach-specific critical dry-weather flows.</p>

Element	Key Findings and Regulatory Provisions																																																												
	<p>Summing the critical flows for each reach and tributary, the critical flow for the entire river is 203 cfs, which is equal to the combined design flow of the three POTWs (169 cfs) plus the median flow from the storm drains and tributaries (34 cfs). The median storm drain and tributary flow is equal to the median flow at Wardlow (145 cfs) minus the existing median POTW flow (111 cfs). The dry-weather loading capacities for each impaired reach include the critical flows for upstream reaches. The dry-weather loading capacity for Reach 5 includes flows from Reach 6 and Bell Creek, the dry-weather loading capacity for Reach 3 includes flows from Verdugo Wash, and the dry-weather loading capacity for Reach 2 includes flows from Arroyo Seco.</p> <p>Dry-weather loading capacity (total recoverable metals)</p> <table><thead><tr><th></th><th>Critical Flow (cfs)</th><th>Cu (kg/day)</th><th>Pb (kg/day)</th><th>Zn (kg/day)</th></tr></thead><tbody><tr><td>LA River Reach 5</td><td>8.74</td><td>0.65</td><td>0.39</td><td></td></tr><tr><td>LA River Reach 4</td><td>129.13</td><td>8.1</td><td>3.2</td><td></td></tr><tr><td>LA River Reach 3</td><td>39.14</td><td>2.3</td><td>1.01</td><td></td></tr><tr><td>LA River Reach 2</td><td>4.44</td><td>0.16</td><td>0.084</td><td></td></tr><tr><td>LA River Reach 1</td><td>2.58</td><td>0.14</td><td>0.075</td><td></td></tr><tr><td>Tujunga Wash</td><td>0.15</td><td>0.007</td><td>0.0035</td><td></td></tr><tr><td>Burbank Channel</td><td>17.3</td><td>0.80</td><td>0.39</td><td></td></tr><tr><td>Rio Hondo Reach 1</td><td>0.50</td><td>0.015</td><td>0.0061</td><td>0.16</td></tr><tr><td>Compton Creek</td><td>0.90</td><td>0.041</td><td>0.020</td><td></td></tr></tbody></table> <p>No dry-weather loading capacities are calculated for lead in Monrovia Canyon Creek or selenium in Reach 6 or its tributaries. Concentration-based allocations are assigned for these metals in these reaches.</p> <p>Wet Weather</p> <p>Wet-weather TMDLs are calculated for cadmium, copper, lead, and zinc in Reach 1. Allocations are developed for all upstream reaches and tributaries to meet these TMDLs.</p> <p>Wet-weather loading capacities are calculated by multiplying daily storm volumes by the wet-weather numeric target for each metal. The resulting curves identify the load allowance for a given flow.</p> <p>Wet-weather loading capacity (total recoverable metals)</p> <table><thead><tr><th>Metal</th><th>Load Duration Curve (kg/day)</th></tr></thead><tbody><tr><td>Cadmium</td><td>Daily storm volume x 3.1 µg/L</td></tr><tr><td>Copper</td><td>Daily storm volume x 17 µg/L</td></tr><tr><td>Lead</td><td>Daily storm volume x 62 µg/L</td></tr><tr><td>Zinc</td><td>Daily storm volume x 159 µg/L</td></tr></tbody></table>		Critical Flow (cfs)	Cu (kg/day)	Pb (kg/day)	Zn (kg/day)	LA River Reach 5	8.74	0.65	0.39		LA River Reach 4	129.13	8.1	3.2		LA River Reach 3	39.14	2.3	1.01		LA River Reach 2	4.44	0.16	0.084		LA River Reach 1	2.58	0.14	0.075		Tujunga Wash	0.15	0.007	0.0035		Burbank Channel	17.3	0.80	0.39		Rio Hondo Reach 1	0.50	0.015	0.0061	0.16	Compton Creek	0.90	0.041	0.020		Metal	Load Duration Curve (kg/day)	Cadmium	Daily storm volume x 3.1 µg/L	Copper	Daily storm volume x 17 µg/L	Lead	Daily storm volume x 62 µg/L	Zinc	Daily storm volume x 159 µg/L
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Load Allocations (for nonpoint sources)	<p>Dry Weather</p> <p>Dry-weather nonpoint source load allocations (LAs) for copper and lead apply to open space and direct atmospheric deposition to the river.</p>																																																												

Element	Key Findings and Regulatory Provisions			
	Dry-weather open space load allocations are equal to the critical flow for the upper portion of tributaries that drain open space, multiplied by the numeric targets for these tributaries.			
	Open space dry-weather LAs (total recoverable metals)			
		Critical Flow	Cu (kg/day)	Pb (kg/day)
	Tujunga Wash	0.12	0.0056	0.0028
	Arroyo Seco	0.33	0.018	0.009
	Load allocations for direct atmospheric deposition to the entire river are obtained from previous studies (3 kg/year for copper, 2 kg/year for lead and 10 kg/year for zinc.) Loads are allocated to each reach and tributary based on their length. The ratio of the length of each river segment to the total length of the river is multiplied by the estimates of direct atmospheric loading to the entire river.			
	Direct air deposition dry-weather LAs (total recoverable metals)			
		Cu (kg/day)	Pb (kg/day)	Zn(kg/day)
	LA River Reach 6	3.3x10 ⁻⁴	2.2x10 ⁻⁴	
	LA River Reach 5	3.6x10 ⁻⁴	2.4x10 ⁻⁴	
	LA River Reach 4	8.1x10 ⁻⁴	5.4x10 ⁻⁴	
	LA River Reach 3	6.04x10 ⁻⁴	4.03x10 ⁻⁴	
	LA River Reach 2	1.4 x10 ⁻³	9.5x10 ⁻⁴	
	LA River Reach 1	4.4x10 ⁻⁴	2.96x10 ⁻⁴	
	Bell Creek	2.98x10 ⁻⁴	1.99x10 ⁻⁴	
	Tujunga Wash	7.4x10 ⁻⁴	4.9x10 ⁻⁴	
	Verdugo Wash	4.7x10 ⁻⁴	3.2x10 ⁻⁴	
Burbank Channel	7.1x10 ⁻⁴	4.7x10 ⁻⁴		
Arroyo Seco	7.3x10 ⁻⁴	4.9x10 ⁻⁴		
Rio Hondo Reach 1	6.4x10 ⁻⁴	4.2x10 ⁻⁴	2.1x10 ⁻³	
Compton Creek	6.5x10 ⁻⁴	4.3x10 ⁻⁴		
A dry-weather concentration-based load allocation for lead equal to the dry-weather numeric target (8.2 µg/L) applies to Monrovia Canyon Creek. The load allocation is not assigned to a particular nonpoint source or group of nonpoint sources.				
A dry-weather concentration-based load allocation for selenium equal to the dry-weather numeric target (5 µg/L) is assigned to Reach 6 and its tributaries. The load allocation is not assigned to a particular nonpoint source or group of nonpoint sources.				
Wet Weather				
Wet-weather load allocations for open space are equal to the percent metals loading from open space (predicted by the wet-weather model) multiplied by the total loading capacity, then by the ratio of open space				

Element	Key Findings and Regulatory Provisions																		
	<p>located outside the storm drain system to the total open space area. There is no load allocation for cadmium because open space is not believed to be a source of the wet-weather cadmium impairment in Reach 1.</p> <p style="text-align: center;">Wet-weather open space LAs (total recoverable metals)</p> <table border="1" data-bbox="630 401 1484 541"> <thead> <tr> <th data-bbox="630 401 792 436">Metal</th><th data-bbox="792 401 1484 436">Load Allocation (kg/day)</th></tr> </thead> <tbody> <tr> <td data-bbox="630 436 792 472">Copper</td><td data-bbox="792 436 1484 472">$2.6 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> <tr> <td data-bbox="630 472 792 508">Lead</td><td data-bbox="792 472 1484 508">$2.4 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> <tr> <td data-bbox="630 508 792 541">Zinc</td><td data-bbox="792 508 1484 541">$1.4 \times 10^{-9} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> </tbody> </table> <p>Wet-weather load allocations for direct atmospheric deposition are equal to the percent area of the watershed comprised by surface water (0.2%) multiplied by the total loading capacity.</p> <p style="text-align: center;">Wet-weather direct air deposition LAs (total recoverable metals)</p> <table border="1" data-bbox="630 709 1484 888"> <thead> <tr> <th data-bbox="630 709 792 745">Metal</th><th data-bbox="792 709 1484 745">Load Allocation (kg/day)</th></tr> </thead> <tbody> <tr> <td data-bbox="630 745 792 781">Cadmium</td><td data-bbox="792 745 1484 781">$6.2 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> <tr> <td data-bbox="630 781 792 816">Copper</td><td data-bbox="792 781 1484 816">$3.4 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> <tr> <td data-bbox="630 816 792 852">Lead</td><td data-bbox="792 816 1484 852">$1.2 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> <tr> <td data-bbox="630 852 792 888">Zinc</td><td data-bbox="792 852 1484 888">$3.2 \times 10^{-9} \mu\text{g /L/day} \times \text{daily storm volume(L)}$</td></tr> </tbody> </table> <p>A wet-weather concentration-based load allocation for selenium equal to the dry-weather numeric target (5 $\mu\text{g/L}$) is assigned to Reach 6 and its tributaries. The load allocation is not assigned to a particular nonpoint source or group of nonpoint sources.</p>	Metal	Load Allocation (kg/day)	Copper	$2.6 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Lead	$2.4 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Zinc	$1.4 \times 10^{-9} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Metal	Load Allocation (kg/day)	Cadmium	$6.2 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Copper	$3.4 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Lead	$1.2 \times 10^{-10} \mu\text{g /L/day} \times \text{daily storm volume(L)}$	Zinc	$3.2 \times 10^{-9} \mu\text{g /L/day} \times \text{daily storm volume(L)}$
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Waste Load Allocations (for point sources)	<p>Dry Weather</p> <p>Dry-weather point source waste load allocations (WLAs) apply to the three POTWs (Tillman, Glendale, and Burbank). A grouped waste load allocation applies to the storm water permittees (Los Angeles County MS4, Long Beach MS4, Caltrans, General Industrial and General Construction), which is calculated by subtracting load allocations (and waste load allocations for reaches with POTWs) from the total loading capacity. Concentration-based waste load allocations are developed for other point sources in the watershed.</p> <p>Mass- and concentration-based waste load allocations for Tillman, Los Angeles-Glendale and Burbank WRPs are developed to meet the dry-weather targets for copper and lead in Reach 4, Reach 3 and the Burbank Western Channel, respectively.</p>																		

Element	Key Findings and Regulatory Provisions				
	POTW dry-weather WLAs (total recoverable metals):				
		Cu	Pb		
	Tillman				
	Concentration-based (µg/L)	26	10		
	Mass-based (kg/day)	7.8	3.03		
	Glendale				
	Concentration-based (µg/L)	26	12		
	Mass-based (kg/day)	2.0	0.88		
	Burbank				
	Concentration-based (µg/L)	19	9.1		
	Mass-based (kg/day)	0.64	0.31		
	Dry-weather waste load allocations for storm water are equal to storm drain flows (critical flows minus median POTW flows minus median open space flows) multiplied by reach-specific numeric targets, minus the contribution from direct air deposition.				
	Storm water dry-weather WLAs (total recoverable metals)				
		Critical Flow (cfs)	Cu (kg/day)	Pb (kg/day)	Zn (kg/day)
	LA River Reach 6	7.20	0.53	0.33	
	LA River Reach 5	0.75	0.05	0.03	
	LA River Reach 4	5.13	0.32	0.12	
	LA River Reach 3	4.84	0.06	0.03	
	LA River Reach 2	3.86	0.13	0.07	
	LA River Reach 1	2.58	0.14	0.07	
	Bell Creek	0.79	0.06	0.04	
	Tujunga Wash	0.03	0.001	0.0002	
	Burbank Channel	3.3	0.15	0.07	
	Verdugo Wash	3.3	0.18	0.10	
	Arroyo Seco	0.25	0.01	0.01	
	Rio Hondo Reach 1	0.50	0.01	0.006	0.16
	Compton Creek	0.90	0.04	0.02	
A zero waste load allocation is assigned to all industrial and construction storm water permittees during dry weather. The remaining waste load allocations are shared by the MS4 permittees and Caltrans.					
Other NPDES Permits					
Concentration-based dry-weather waste load allocations apply to the other NPDES permits* that discharge to the reaches and tributaries in the following table. * “Other NPDES permits” refers to minor NPDES permits, general non-storm water NDPES permits, and major permits other than the Tillman, LA-Glendale, and Burbank POTWs.					

Element	Key Findings and Regulatory Provisions			
	Other dry-weather WLAs (µg total recoverable metals/L)			
		Cu	Pb	Zn Se
	Reach 5, 6	30	19	5
	Reach 4	26	10	
	Reach 3 above LA-Glendale WRP and Verdugo	23	12	
	Reach 3 below LA-Glendale WRP	26	12	
	Burbank Western Channel(above WRP)	26	14	
	Burbank Western Channel (below WRP)	19	9.1	
	Reach 2			
	and Arroyo Seco	22	11	
	Reach 1	23	12	
	Compton Creek	19	8.9	
	Rio Hondo Reach 1	13	5.0	131
	<p>Wet Weather During wet-weather, POTW allocations are based on dry-weather in-stream numeric targets because the POTWs exert the greatest influence over in-stream water quality during dry weather. During wet weather, the concentration-based dry-weather waste load allocations apply but the mass-based dry-weather allocations do not apply when influent flows exceed the design capacity of the treatment plants. Additionally, the POTWs are assigned reach-specific allocations for cadmium and zinc based on dry weather targets to meet the wet-weather TMDLs in Reach 1.</p>			
	POTW wet-weather WLAs (total recoverable metals):			
		Cd	Cu	Pb Zn
	Tillman			
	Concentration-based (µg/L)	4.7	26	10 212
	Mass-based (kg/day)	1.4	7.8	3.03 64
	Glendale			
	Concentration-based (µg/L)	5.3	26	12 253
	Mass-based (kg/day)	0.40	2.0	0.88 19
	Burbank			
	Concentration-based (µg/L)	4.5	19	9.1 212
	Mass-based (kg/day)	0.15	0.64	0.31 7.3

Element	Key Findings and Regulatory Provisions																																																		
	<p>Wet-weather waste load allocations for the grouped storm water permittees are equal to the total loading capacity minus the load allocations for open space and direct air deposition and the waste load allocations for the POTWs. Wet-weather waste load allocations for the grouped storm water permittees apply to all reaches and tributaries.</p> <p>Storm water wet-weather WLAs (total recoverable metals):</p> <table> <tr> <th>Metal</th><th>Waste Load Allocation (kg/day)</th></tr> <tr> <td>Cadmium</td><td>3.1×10^{-9} x daily volume(L) – 1.95</td></tr> <tr> <td>Copper</td><td>1.7×10^{-8} x daily volume (L) – 10</td></tr> <tr> <td>Lead</td><td>6.2×10^{-8} x daily volume (L) – 4.2</td></tr> <tr> <td>Zinc</td><td>1.6×10^{-7} x daily volume (L) – 90</td></tr> </table> <p>The combined storm water waste load allocation is apportioned between the different storm water categories by their percent area of the portion of the watershed served by storm drains.</p> <p>MS4 wet-weather WLAs (total recoverable metals):</p> <table> <tr> <th>Metal</th><th>Waste Load Allocation (kg/day)</th></tr> <tr> <td>Cadmium</td><td>2.8×10^{-9} x daily volume(L) – 1.8</td></tr> <tr> <td>Copper</td><td>1.5×10^{-8} x daily volume (L) – 9.5</td></tr> <tr> <td>Lead</td><td>5.6×10^{-8} x daily volume (L) – 3.85</td></tr> <tr> <td>Zinc</td><td>1.4×10^{-7} x daily volume (L) – 83</td></tr> </table> <p>Caltrans wet-weather WLAs (total recoverable metals):</p> <table> <tr> <th>Metal</th><th>Waste Load Allocation (kg/day)</th></tr> <tr> <td>Cadmium</td><td>5.3×10^{-11} x daily volume(L) – 0.03</td></tr> <tr> <td>Copper</td><td>2.9×10^{-10} x daily volume (L) – 0.2</td></tr> <tr> <td>Lead</td><td>1.06×10^{-9} x daily volume (L) – 0.07</td></tr> <tr> <td>Zinc</td><td>2.7×10^{-9} x daily volume (L) – 1.6</td></tr> </table> <p>General Industrial wet-weather WLAs (total recoverable metals):</p> <table> <tr> <th>Metal</th><th>Waste Load Allocation (kg/day)</th></tr> <tr> <td>Cadmium</td><td>1.6×10^{-10} x daily volume(L) – 0.11</td></tr> <tr> <td>Copper</td><td>8.8×10^{-10} x daily volume (L) – 0.5</td></tr> <tr> <td>Lead</td><td>3.3×10^{-9} x daily volume (L) – 0.22</td></tr> <tr> <td>Zinc</td><td>8.3×10^{-9} x daily volume (L) – 4.8</td></tr> </table> <p>General Construction wet-weather WLAs (total recoverable metals):</p> <table> <tr> <th>Metal</th><th>Waste Load Allocation (kg/day)</th></tr> <tr> <td>Cadmium</td><td>5.9×10^{-11} x daily volume(L) – 0.04</td></tr> <tr> <td>Copper</td><td>3.2×10^{-10} x daily volume (L) – 0.2</td></tr> <tr> <td>Lead</td><td>1.2×10^{-9} x daily volume (L) – 0.08</td></tr> <tr> <td>Zinc</td><td>3.01×10^{-9} x daily volume (L) – 4.8</td></tr> </table> <p>Each storm water permittee under the general industrial and construction storm water permits will receive individual waste load allocations per acre based on the total acres of their facility.</p>	Metal	Waste Load Allocation (kg/day)	Cadmium	3.1×10^{-9} x daily volume(L) – 1.95	Copper	1.7×10^{-8} x daily volume (L) – 10	Lead	6.2×10^{-8} x daily volume (L) – 4.2	Zinc	1.6×10^{-7} x daily volume (L) – 90	Metal	Waste Load Allocation (kg/day)	Cadmium	2.8×10^{-9} x daily volume(L) – 1.8	Copper	1.5×10^{-8} x daily volume (L) – 9.5	Lead	5.6×10^{-8} x daily volume (L) – 3.85	Zinc	1.4×10^{-7} x daily volume (L) – 83	Metal	Waste Load Allocation (kg/day)	Cadmium	5.3×10^{-11} x daily volume(L) – 0.03	Copper	2.9×10^{-10} x daily volume (L) – 0.2	Lead	1.06×10^{-9} x daily volume (L) – 0.07	Zinc	2.7×10^{-9} x daily volume (L) – 1.6	Metal	Waste Load Allocation (kg/day)	Cadmium	1.6×10^{-10} x daily volume(L) – 0.11	Copper	8.8×10^{-10} x daily volume (L) – 0.5	Lead	3.3×10^{-9} x daily volume (L) – 0.22	Zinc	8.3×10^{-9} x daily volume (L) – 4.8	Metal	Waste Load Allocation (kg/day)	Cadmium	5.9×10^{-11} x daily volume(L) – 0.04	Copper	3.2×10^{-10} x daily volume (L) – 0.2	Lead	1.2×10^{-9} x daily volume (L) – 0.08	Zinc	3.01×10^{-9} x daily volume (L) – 4.8
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Element	Key Findings and Regulatory Provisions																		
	<p>Individual General Construction or Industrial Permittees WLAs</p> <p>(total recoverable metals):</p> <table><tr><th>Metal</th><th>Waste Load Allocation (g/day/acre)</th></tr><tr><td>Cadmium</td><td>7.6×10^{-12} x daily volume(L) – 4.8×10^{-6}</td></tr><tr><td>Copper</td><td>4.2×10^{-11} x daily volume (L) – 2.6×10^{-5}</td></tr><tr><td>Lead</td><td>1.5×10^{-10} x daily volume (L) – 1.04×10^{-5}</td></tr><tr><td>Zinc</td><td>3.9×10^{-10} x daily volume (L) – 2.2×10^{-4}</td></tr></table> <p>Other NPDES Permits Concentration-based wet-weather waste load allocations apply to the other NPDES permits* that discharge to all reaches of the Los Angeles River and its tributaries.</p> <p>Wet-weather WLAs for other permits (total recoverable metals)</p> <table><tr><th>Cadmium (µg /L)</th><th>Copper (µg /L)</th><th>Lead (µg /L)</th><th>Zinc (µg /L)</th></tr><tr><td>3.1</td><td>17</td><td>62</td><td>159</td></tr></table> <p>* “Other NPDES permits” refers to minor NPDES permits, general non-storm water ND PES permits, and major permits other than the Tillman, LA-Glendale, and Burbank POTWs.</p>	Metal	Waste Load Allocation (g/day/acre)	Cadmium	7.6×10^{-12} x daily volume(L) – 4.8×10^{-6}	Copper	4.2×10^{-11} x daily volume (L) – 2.6×10^{-5}	Lead	1.5×10^{-10} x daily volume (L) – 1.04×10^{-5}	Zinc	3.9×10^{-10} x daily volume (L) – 2.2×10^{-4}	Cadmium (µg /L)	Copper (µg /L)	Lead (µg /L)	Zinc (µg /L)	3.1	17	62	159
Metal	Waste Load Allocation (g/day/acre)																		
Cadmium	7.6×10^{-12} x daily volume(L) – 4.8×10^{-6}																		
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Margin of Safety	<p>There is an implicit margin of safety that stems from the use of conservative values for the translation from total recoverable to the dissolved fraction during the dry and wet periods. In addition, the TMDL includes a margin of safety by evaluating wet-weather conditions separately from dry-weather conditions, which is in effect, assigning allocations for two distinct critical conditions. Furthermore, the use of the wet-weather model to calculate load allocations for open space can be applied to the margin of safety because it tends to overestimate loads from open spaces, thus reducing the available waste load allocations to the permitted discharges.</p>																		
Implementation	<p>The regulatory mechanisms used to implement the TMDL will include the Los Angeles County Municipal Storm Water NPDES Permit (MS4), the City of Long Beach MS4, the Caltrans storm water permit, major NPDES permits, minor NPDES permits, general NPDES permits, general industrial storm water NPDES permits, and general construction storm water NPDES permits. Nonpoint sources will be regulated through the authority contained in sections 13263 and 13269 of the Water Code, in conformance with the State Water Resources Control Board’s Nonpoint Source Implementation and Enforcement Policy (May 2004). Each NPDES permit assigned a WLA shall be reopened or amended at reissuance, in accordance with applicable laws, to incorporate the applicable WLAs as a permit requirement.</p> <p>The Regional Board shall reconsider this TMDL in five years after the effective date of the TMDL based on additional data obtained from special studies. Table 7-13-2 presents the implementation schedule for the responsible permittees.</p>																		

Element	Key Findings and Regulatory Provisions
	<p data-bbox="634 218 1471 283">Non storm water NPDES permits (including POTWs, other major, minor, and general permits):</p> <p data-bbox="634 321 1542 751">Permit writers may translate applicable waste load allocations into effluent limits for the major, minor and general NPDES permits by applying the effluent limitation procedures in Section 1.4 of the State Water Resources Control Board’s Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California (2000) or other applicable engineering practices authorized under federal regulations. Compliance schedules may be established in individual NPDES permits, allowing up to 5 years within a permit cycle to achieve compliance. Compliance schedules may not be established in general NPDES permits. A discharger that can not comply immediately with effluent limitations specified to implement waste load allocations will be required to apply for an individual permit in order to demonstrate the need for a compliance schedule.</p> <p data-bbox="634 774 1542 940">If a POTW demonstrates that advanced treatment (necessitating long design and construction timeframes) will be required to meet final waste load allocations, the Regional Board will consider extending the implementation schedule to allow the POTW up to 10 years from the effective date of the TMDL to achieve compliance with the final WLAs.</p> <p data-bbox="634 963 1542 1094">Permittees that hold individual NPDES permits and solely discharge storm water may be allowed (at Regional Board discretion) compliance schedules up to 10 years from the effective date of the TMDL to achieve compliance with final WLAs.</p> <p data-bbox="634 1117 1138 1148">General industrial storm water permits:</p> <p data-bbox="634 1171 1542 1236">The Regional Board will develop a watershed-specific general industrial storm water permit to incorporate waste load allocations.</p> <p data-bbox="634 1260 976 1291">Dry-weather implementation</p> <p data-bbox="634 1314 1542 1543">Non-storm water flows authorized by Order No. 97-03 DWQ, or any successor order, are exempt from the dry-weather waste load allocation equal to zero. Instead, these authorized non-storm water flows shall meet the reach-specific concentration-based waste load allocations assigned to the “other NPDES permits”. The dry-weather waste load allocation equal to zero applies to unauthorized non-storm water flows, which are prohibited by Order No. 97-03 DWQ.</p> <p data-bbox="634 1566 1542 1795">It is anticipated that the dry-weather waste load allocations will be implemented by requiring improved best management practices (BMPs) to eliminate the discharge of non-storm water flows. However, permit writers must provide adequate justification and documentation to demonstrate that specified BMPs are expected to result in attainment of the numeric waste load allocations.</p>

Element	Key Findings and Regulatory Provisions												
	<p><u>Wet-weather implementation</u></p> <p>General industrial storm water permittees are allowed interim wet-weather concentration-based waste load allocations based on benchmarks contained in EPA’s Storm Water Multi-sector General Permit for Industrial Activities. The interim waste load allocations apply to all industry sectors and apply for a period not to exceed ten years from the effective date of the TMDL.</p> <table><tr><th colspan="4">Interim wet-weather WLAs for general industrial storm water permittees (total recoverable metals)*</th></tr><tr><th>Cd (µg/L)</th><th>Cu(µg/L)</th><th>Pb(µg/L)</th><th>Zn(µg/L)</th></tr><tr><td>15.9</td><td>63.6</td><td>81.6</td><td>117</td></tr></table> <p>*Based on USEPA benchmarks for industrial storm water sector</p> <p>In the first five years from the effective date of the TMDL, interim waste load allocations will not be interpreted as enforceable permit conditions. If monitoring demonstrates that interim waste load allocations are being exceeded, the permittee shall evaluate existing and potential BMPs, including structural BMPs, and implement any necessary BMP improvements. It is anticipated that monitoring results and any necessary BMP improvements would occur as part of an annual reporting process. After five years from the effective date of the TMDL, interim waste load allocations shall be translated into enforceable permit conditions. Compliance with permit conditions may be demonstrated through the installation, maintenance, and monitoring of Regional Board-approved BMPs. If this method of compliance is chosen, permit writers must provide adequate justification and documentation to demonstrate that BMPs are expected to result in attainment of interim waste load allocations.</p> <p>The general industrial storm water permits shall achieve final wet-weather waste load allocations no later than 10 years from the effective date of the TMDL, which shall be expressed as NPDES water quality-based effluent limitations. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs if adequate justification and documentation demonstrate that BMPs are expected to result in attainment of waste load allocations.</p> <p>General construction storm water permits:</p> <p>Waste load allocations will be incorporated into the State Board general permit upon renewal or into a watershed-specific general permit developed by the Regional Board.</p> <p>Dry-weather implementation</p> <p>Non-storm water flows authorized by the General Permit for Storm Water Discharges Associated with Construction Activity (Water Quality Order No. 99-08 DWQ), or any successor order, are exempt from the dry-weather waste load allocation equal to zero as long as they</p>	Interim wet-weather WLAs for general industrial storm water permittees (total recoverable metals)*				Cd (µg/L)	Cu(µg/L)	Pb(µg/L)	Zn(µg/L)	15.9	63.6	81.6	117
Interim wet-weather WLAs for general industrial storm water permittees (total recoverable metals)*													
Cd (µg/L)	Cu(µg/L)	Pb(µg/L)	Zn(µg/L)										
15.9	63.6	81.6	117										

Element	Key Findings and Regulatory Provisions
	<p>comply with the provisions of sections C.3.and A.9 of the Order No. 99-08 DWQ, which state that these authorized non-storm discharges shall be (1) infeasible to eliminate (2) comply with BMPs as described in the Storm Water Pollution Prevention Plan prepared by the permittee, and (3) not cause or contribute to a violation of water quality standards, or comparable provisions in any successor order. Unauthorized non-storm water flows are already prohibited by Order No. 99-08 DWQ.</p> <p><u>Wet-weather implementation</u></p> <p>Within seven years of the effective date of the TMDL, the construction industry will submit the results of BMP effectiveness studies to determine BMPs that will achieve compliance with the final waste load allocations assigned to construction storm water permittees. Regional Board staff will bring the recommended BMPs before the Regional Board for consideration within eight years of the effective date of the TMDL. General construction storm water permittees will be considered in compliance with final waste load allocations if they implement these Regional Board approved BMPs. All permittees must implement the approved BMPs within nine years of the effective date of the TMDL. If no effectiveness studies are conducted and no BMPs are approved by the Regional Board within eight years of the effective date of the TMDL, each general construction storm water permit holder will be subject to site-specific BMPs and monitoring requirements to demonstrate compliance with final waste load allocations.</p> <p>MS4 and Caltrans permits</p> <p>Applicable CTR limits are being met most of the time during dry weather, with episodic exceedances. Due to the expense of obtaining accurate flow measurements required for calculating loads, concentration-based permit limits may apply during dry weather. These concentration-based limits would be equal to dry-weather reach-specific numeric targets.</p> <p>Each municipality and permittee will be required to meet the storm water waste load allocations shared by the two MS4s and Caltrans permittees at the designated TMDL effectiveness monitoring points. A phased implementation approach, using a combination of non-structural and structural BMPs may be used to achieve compliance with the waste load allocations. The administrative record and the fact sheets for the MS4 and Caltrans storm water permits must provide reasonable assurance that the BMPs selected will be sufficient to implement the waste load allocations.</p> <p>The implementation schedule for the MS4 and Caltrans permittees consists of a phased approach. The watershed is divided into five jurisdictional groups based on the subwatersheds of the tributaries that drain to each reach of the river, as presented in Table 7-13-3. Each</p>

Element	Key Findings and Regulatory Provisions
	<p>jurisdictional group shall achieve compliance in prescribed percentages of its subwatershed(s), with total compliance to be achieved within 22 years. Jurisdictional groups can be reorganized or subdivided upon approval by the Executive Officer.</p>
<p><i>Seasonal Variations and Critical Conditions</i></p>	<p>Seasonal variations are addressed by developing separate waste load allocations for dry weather and wet weather.</p> <p>For dry weather, critical flows for each reach are established from the long-term flow records (1988-2000) generated by stream gages located throughout the watershed and in selected reaches. The median dry-weather urban runoff plus the combined design capacity of the three major POTWs is selected as the critical flow since most of the flow is from effluent which results in a relatively stable dry-weather flow condition. In areas where there are no flow records, an area-weighted approach is used to assign flows to these reaches.</p> <p>Wet-weather allocations are developed using the load-duration curve concept. The total wet-weather waste load allocation for wet weather varies by storm. Given this variability in storm water flows, no justification was found for selecting a particular sized storm as the critical condition.</p>
<p><i>Compliance Monitoring and Special Studies</i></p>	<p>Effective monitoring will be necessary to assess the condition of the Los Angeles River and its tributaries and to assess the on-going effectiveness of efforts by dischargers to reduce metals loading to the Los Angeles River. Special studies may also be appropriate to provide further information about new data, new or alternative sources, and revised scientific assumptions. Below the Regional Board identifies the various goals of monitoring efforts and studies. The programs, reports, and studies will be developed in response to subsequent orders issued by the Executive Officer.</p> <p>Ambient Monitoring</p> <p>An ambient monitoring program is necessary to assess water quality throughout the Los Angeles River and its tributaries and the progress being made to remove the metals impairments. The MS4 and Caltrans storm water NPDES permittees in each jurisdictional group are jointly responsible for implementing the ambient monitoring program. The responsible agencies shall sample for total recoverable metals, dissolved metals, including cadmium and zinc, and hardness once per month at each ambient monitoring location at least until the TMDL is re-considered at year 5. The reported detection limits shall be below the hardness adjusted CTR criteria. Eight ambient monitoring points currently exist in the Los Angeles River and its tributaries as part of the City of Los Angeles Watershed Monitoring Program. These monitoring points could be used to assess water quality.</p>

Element	Key Findings and Regulatory Provisions																		
	<p>Ambient Monitoring Points</p> <table border="0"> <thead> <tr> <th></th><th>Reaches and Tributaries</th></tr> </thead> <tbody> <tr> <td>White Oak Avenue</td><td>LA River 6, Aliso Creek, McCoy Creek, Bell Creek</td></tr> <tr> <td>Sepulveda Boulevard</td><td>LA River 5, Bull Creek</td></tr> <tr> <td>Tujunga Avenue</td><td>LA River 4, Tujunga Wash</td></tr> <tr> <td>Colorado Boulevard</td><td>LA River 3, Burbank Western Channel, Verdugo Wash</td></tr> <tr> <td>Figueroa Street</td><td>LA River 3, Arroyo Seco</td></tr> <tr> <td>Washington Boulevard</td><td>LA River 2</td></tr> <tr> <td>Rosecrans Avenue</td><td>LA River 2, Rio Hondo (gage just above Rio Hondo)</td></tr> <tr> <td>Willow</td><td>LA River 1, Compton Creek (gage at Wardlow) Street</td></tr> </tbody> </table> <p>TMDL Effectiveness Monitoring</p> <p>The MS4 and Caltrans storm water NPDES permittees in each jurisdictional group are jointly responsible for assessing progress in reducing pollutant loads to achieve the TMDL. Each jurisdictional group is required to submit for approval by the Executive Officer a coordinated monitoring plan that will demonstrate the effectiveness of the phased implementation schedule for this TMDL (See Table 7-13.2), which requires attainment of the applicable waste load allocations in prescribed percentages of each subwatershed over a 22-year period. The monitoring locations specified for the ambient monitoring program may be used as effectiveness monitoring locations.</p> <p>The MS4 and Caltrans storm water NPDES permittees will be found to be effectively meeting dry-weather waste load allocations if the in-stream pollutant concentration or load at the first downstream monitoring location is equal to or less than the corresponding concentration- or load-based waste load allocation. Alternatively, effectiveness of the TMDL may be assessed at the storm drain outlet based on the waste load allocation for the receiving water. For storm drains that discharge to other storm drains, the waste load allocation will be based on the waste load allocation for the ultimate receiving water for that storm drain system. The MS4 and Caltrans storm water NPDES permittees will be found to be effectively meeting wet-weather waste load allocations if the loading at the downstream monitoring location is equal to or less than the wet-weather waste load allocation.</p> <p>The general industrial storm water permit shall contain a model monitoring and reporting program to evaluate BMP effectiveness. A permittee enrolled under the general permit shall have the choice of conducting individual monitoring based on the model program or participating in a group monitoring effort. MS4 permittees are</p>		Reaches and Tributaries	White Oak Avenue	LA River 6, Aliso Creek, McCoy Creek, Bell Creek	Sepulveda Boulevard	LA River 5, Bull Creek	Tujunga Avenue	LA River 4, Tujunga Wash	Colorado Boulevard	LA River 3, Burbank Western Channel, Verdugo Wash	Figueroa Street	LA River 3, Arroyo Seco	Washington Boulevard	LA River 2	Rosecrans Avenue	LA River 2, Rio Hondo (gage just above Rio Hondo)	Willow	LA River 1, Compton Creek (gage at Wardlow) Street
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Willow	LA River 1, Compton Creek (gage at Wardlow) Street																		

Element	Key Findings and Regulatory Provisions
	<p>encouraged to take the lead in group monitoring efforts for industrial facilities within their jurisdiction because compliance with waste load allocations by these facilities will in many cases translate to reductions in metals loads to the MS4 system.</p> <p>The Tillman, LA-Glendale, and Burbank POTWs, and the remaining permitted discharges in the watershed will have effluent monitoring requirements to ensure compliance with waste load allocations.</p> <p>Special Studies</p> <p>The implementation schedule (see Table 7-13.2) allows time for special studies that may serve to refine the estimate of loading capacity, waste load and/or load allocations, and other studies that may serve to optimize implementation efforts. The Regional Board will re-consider the TMDL in the fifth year after the effective date in light of the findings of these studies. Studies may include:</p> <ul style="list-style-type: none"> . • Refined flow estimates for the Los Angeles River mainstem and tributaries where there presently are no flow gages and for improved gaging of low-flow conditions. . • Water quality measurements, including a better assessment of hardness, water chemistry data (e.g., total suspended solids and organic carbon) that may refine the use of metals partitioning coefficients. . • Effects studies designed to evaluate site-specific toxic effects of metals on the Los Angeles River and its tributaries. . • Source studies designed to characterize loadings from background or natural sources . • Review of water quality modeling assumptions including the relationship between metals and total suspended solids as expressed in the potency factors and buildup and washoff and transport coefficients. . • Evaluation of aerial deposition and sources of aerial deposition. . • POTWs that are unable to demonstrate compliance with final waste load allocations must conduct source reduction audits within two years of the effective date of the TMDL. . • POTWs that will be requesting the Regional Board to extend their implementation schedule to allow for the installation of advanced treatment must prepare work plans, with time schedules to allow for the installation advanced treatment. The work plan must be submitted within four years from the effective date of the TMDL.

Table 7-13.2 Los Angeles River and Tributaries Metals TMDL: Implementation Schedule

Date	Action
Effective date of TMDL	Regional Board permit writers shall incorporate waste load allocations into NPDES permits. Waste load allocations will be implemented through NPDES permit limits in accordance with the implementation schedule contained herein, at the time of permit issuance, renewal, or re-opener.
4 years after effective date of the TMDL	Responsible jurisdictions and agencies shall provide to the Regional Board results of the special studies. POTWs that will be requesting the Regional Board to extend their implementation schedule to allow for the installation of advanced treatment must submit work plans.
5 years after effective date of the TMDLs	The Regional Board shall reconsider this TMDL to re-evaluate the waste load allocations and the implementation schedule.
NON-STORM WATER NPDES PERMITS (INCLUDING POTWS, OTHER MAJOR, MINOR, AND GENERAL PERMITS)	
Upon permit issuance, renewal, or re-opener	The non-storm water NPDES permits shall achieve waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Compliance schedules may allow up to 5 years in individual NPDES permits to meet permit requirements. Compliance schedules may not be established in general NPDES permits. If a POTW demonstrates that advanced treatment will be required to meet final waste load allocations, the Regional Board will consider extending the implementation schedule to allow the POTW up to 10 years from the effective date of the TMDL to achieve compliance with the final WLAs. Permittees that hold individual NPDES permits and solely discharge storm water may be allowed (at Regional Board discretion) compliance schedules up to 10 years from the effective date of the TMDL to achieve compliance with final WLAs.
GENERAL INDUSTRIAL STORM WATER PERMITS	
Upon permit issuance, renewal, or re-opener	The general industrial storm water permittees shall achieve dry-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs. Permittees shall begin to install and test BMPs to meet the interim wet-weather WLAs. BMP effectiveness monitoring will be implemented to determine progress in achieving interim wet-weather waste load allocations.

Date	Action
5 years after effective date of the TMDLs	The general industrial storm water permits shall achieve interim wet-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs. Permittees shall begin an iterative BMP process including BMP effectiveness monitoring to achieve compliance with final waste load allocations.
10 years after the effective date of TMDL	The general industrial storm water permits shall achieve final wet-weather waste load allocations, which shall be expressed as NPDES water quality-based effluent limitations. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs.
GENERAL CONSTRUCTION STORM WATER PERMITS	
Upon permit issuance, renewal, or re-opener	Non-storm water flows not authorized by Order No. 99-08 DWQ, or any successor order, shall achieve dry-weather waste load allocations of zero. Waste load allocations shall be expressed as NPDES water quality-based effluent limitations specified in accordance with federal regulations and state policy on water quality control. Effluent limitations may be expressed as permit conditions, such as the installation, maintenance, and monitoring of Regional Board-approved BMPs.
Seven years from the effective date of the TMDL	The construction industry will submit the results of wet-weather BMP effectiveness studies to the Regional Board for consideration. In the event that no effectiveness studies are conducted and no BMPs are approved, permittees shall be subject to site-specific BMPs and monitoring to demonstrate BMP effectiveness.
Eight years from the effective date of the TMDL	The Regional Board will consider results of the wet-weather BMP effectiveness studies and consider approval of BMPs no later than eight years from the effective date of the TMDL.
Nine years from the effective date of the TMDL	All general construction storm water permittees shall implement Regional Board-approved BMPs.
MS4 AND CALTRANS STORM WATER PERMITS	
15 months after the effective date of the TMDL	In response to an order issued by the Executive Officer, each jurisdictional group must submit a coordinated monitoring plan, to be approved by the Executive Officer, which includes both TMDL effectiveness monitoring and ambient monitoring. Once the coordinated monitoring plan is approved by the Executive Officer ambient monitoring shall commence.

Date	Action
48 months after effective date of TMDL (Draft Report) 54 months after effective date of TMDL (Final Report)	Each jurisdictional group shall provide a written report to the Regional Board outlining the how the subwatersheds within the jurisdictional group will achieve compliance with the waste load allocations. The report shall include implementation methods, an implementation schedule, proposed milestones, and any applicable revisions to the TMDL effectiveness monitoring plan.
6 years after effective date of the TMDL	Each jurisdictional group shall demonstrate that 50% of the group's total drainage area served by the storm drain system is effectively meeting the dry-weather waste load allocations and 25% of the group's total drainage area served by the storm drain system is effectively meeting the wet-weather waste load allocations.
14 years after effective date of the TMDL	Each jurisdictional group shall demonstrate that 75% of the group's total drainage area served by the storm drain system is effectively meeting the dry-weather WLAs.
18 years after effective date of the TMDL	Each jurisdictional group shall demonstrate that 100% of the group's total drainage area served by the storm drain system is effectively meeting the dry-weather WLAs and 50% of the group's total drainage area served by the storm drain system is effectively meeting the wet-weather WLAs.
22 years after effective date of the TMDL	Each jurisdictional group shall demonstrate that 100% of the group's total drainage area served by the storm drain system is effectively meeting both the dry-weather and wet-weather WLAs.

Table 7-13.3 Los Angeles River and Tributaries Metals TMDL: Jurisdictional Groups
Jurisdictional Group

	Responsible Jurisdictions & Agencies		Subwatershed(s)
1	Carson County of Los Angeles City of Los Angeles Compton Huntington Park Long Beach Lynwood Signal Hill Southgate Vernon		Los Angeles River Reach 1 and Compton Creek
2	Alhambra Arcadia Bell Bellflower Bell Gardens Bradbury Carson Commerce Compton County of Los Angeles Cudahy Downey Duarte El Monte Glendale Huntington Park Irwindale La Canada Flintridge Vernon	Long Beach City of Los Angeles Lynwood Maywood Monrovia Montebello Monterey Park Paramount Pasadena Pico Rivera Rosemead San Gabriel San Marino Sierra Madre South El Monte South Pasadena Southgate Temple City	Los Angeles River Reach 2, Rio Hondo, Arroyo Seco, and all contributing sub watersheds
3	City of Los Angeles County of Los Angeles Burbank Glendale Pasadena	La Canada Flintridge	Los Angeles River Reach 3, Verdugo Wash, Burbank Western Channel
4-5	Burbank Glendale City of Los Angeles County of Los Angeles San Fernando		Los Angeles River Reach 4, Reach 5, Tujunga Wash, and all contributing subwatersheds
6	Calabasas City of Los Angeles County of Los Angeles Hidden Hills		Los Angeles River Reach 6, Bell Creek, and all contributing subwatersheds

APPENDIX C

Summary of Compliance Monitoring Locations

Los Angeles River Metals TMDL Water Quality Monitoring Locations

Tier I – Ambient & Effectiveness Locations

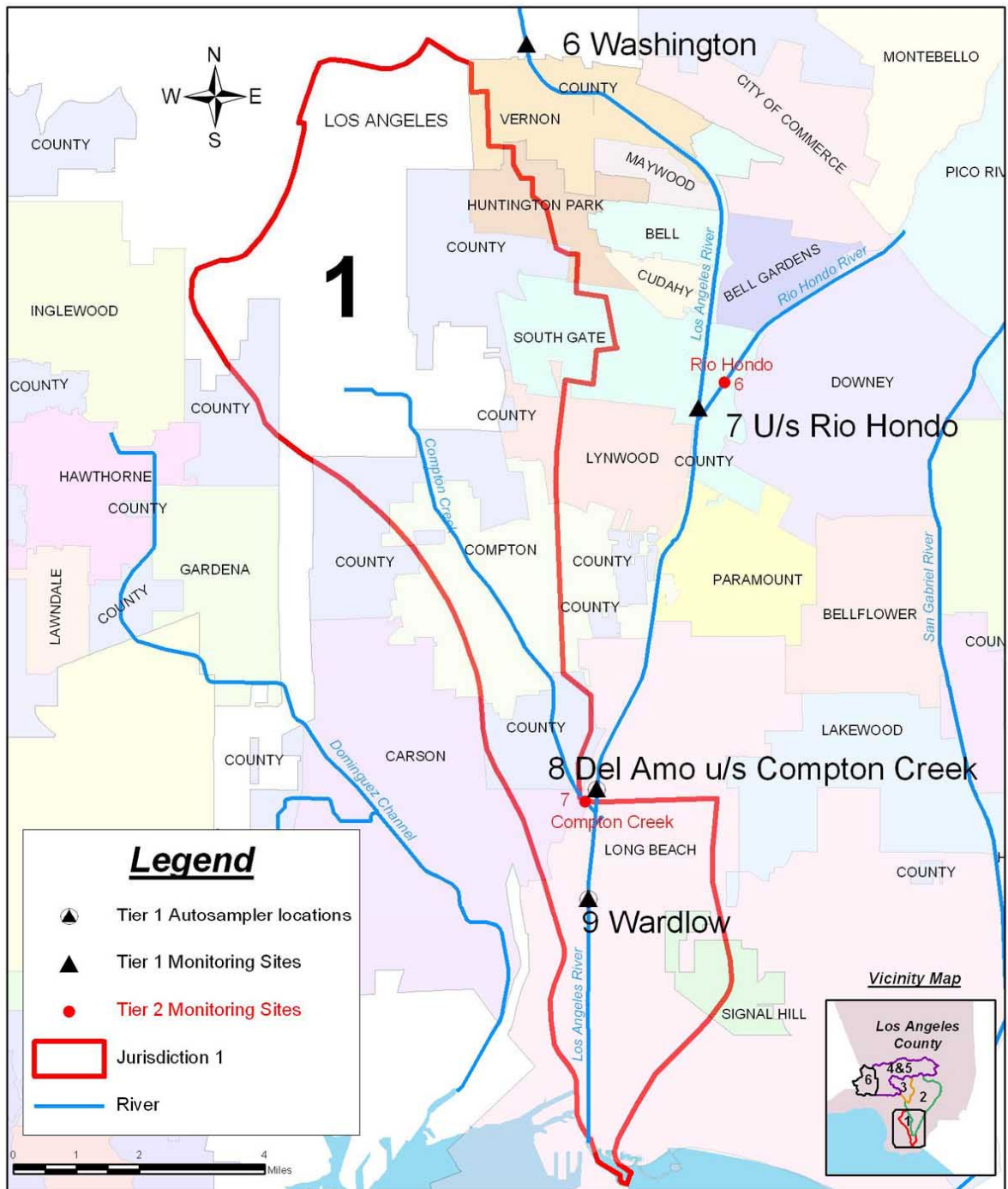
Monitoring Location	TMDL Addressed	Jurisdiction	Location	Freq	Lat.	Long.	Percentage of Watershed	TBG Map	Comments
LAR – 1	Metals	6	Main Channel	Monthly	34.185076°	-118.518735°	13.4%	531-B7	@ White Oak
LAR – 2	Metals	4/5	Main Channel	Monthly	34.161559°	-118.465969°	18.6%	561- H3	@ Sepulveda
LAR – 3	Metals	4/5	Main Channel	Monthly	34.140977°	-118.379127°	48.4%	562-J6	@ Tujunga
LAR – 4	Metals	3	Main Channel	Monthly	34.140863°	-118.276523°	59.3%	564-C5	@ Colorado
LAR – 5	Metals	3	Main Channel	Monthly	34.081249°	-118.227546°	61.4%	594-H7	@ Figueroa upstream of the Arroyo Seco
LAR – 6	Metals	2	Main Channel	Monthly	34.017325°	-118.223783°	69.3%	674-J1	@ Washington
LAR – 7	Metals	2	Main Channel	Monthly	33.934206°	-118.175479°	73.2%	705-F6	U/S Rio Hondo
LAR – 8	Metals	2	Main Channel	Monthly	33.846228°	-118.203295°	93.2%	765-C4	@ Del Amo Ave.
LAR – 9	Metals	1	Main Channel	Monthly	33.819002°	-118.205560°	98.7%	765-C7	@ Wardlow Ave.

Los Angeles River Metals TMDL Water Quality Monitoring Locations

Tier II – Upstream Locations

Monitoring Location	TMDL Addressed	Jurisdiction	Location	Freq	Lat.	Long.	Percentage of Watershed	TBG Map	Comments
LAR2 – 1	Metals	6	Main Channel D/S Confluence	As needed*	34.195135°	-118.59763°	4.8%	530-B6	@ Canoga Ave.
LAR2 – 2	Metals	4/5	Tujunga Wash	As needed*	34.150429°	-118.39312°	26.32%	562-G4	@ Moorpark Ave.
LAR2 – 3	Metals	3	Burbank Western Channel.	As needed*	34.160714°	-118.30502°	3.0%	562-J3	@ Riverside Dr
LAR2 – 4	Metals	3	Verdugo Wash	As needed*	34.156700°	-118.27115°	3.6%	564-C3	@ Concord St.
LAR2 – 5	Metals	2	Arroyo Seco	As needed*	34.080470°	-118.22496°	5.6%	594-F2	@ San Fernando Rd.
LAR2 – 6	Metals	2	Rio Hondo	As needed*	34.154869°	-118.27604°	16.7%	705-G5	@ Garfield Ave.
LAR2 – 7	Metals	1	Compton Creek.	As needed*	33.846214°	-118.20899°	5%	765-B4	@ Del Amo Blvd

* Tier II activation criteria is 3 consecutive exceedances of the Waste Load Allocation(s) at a Tier I monitoring site.





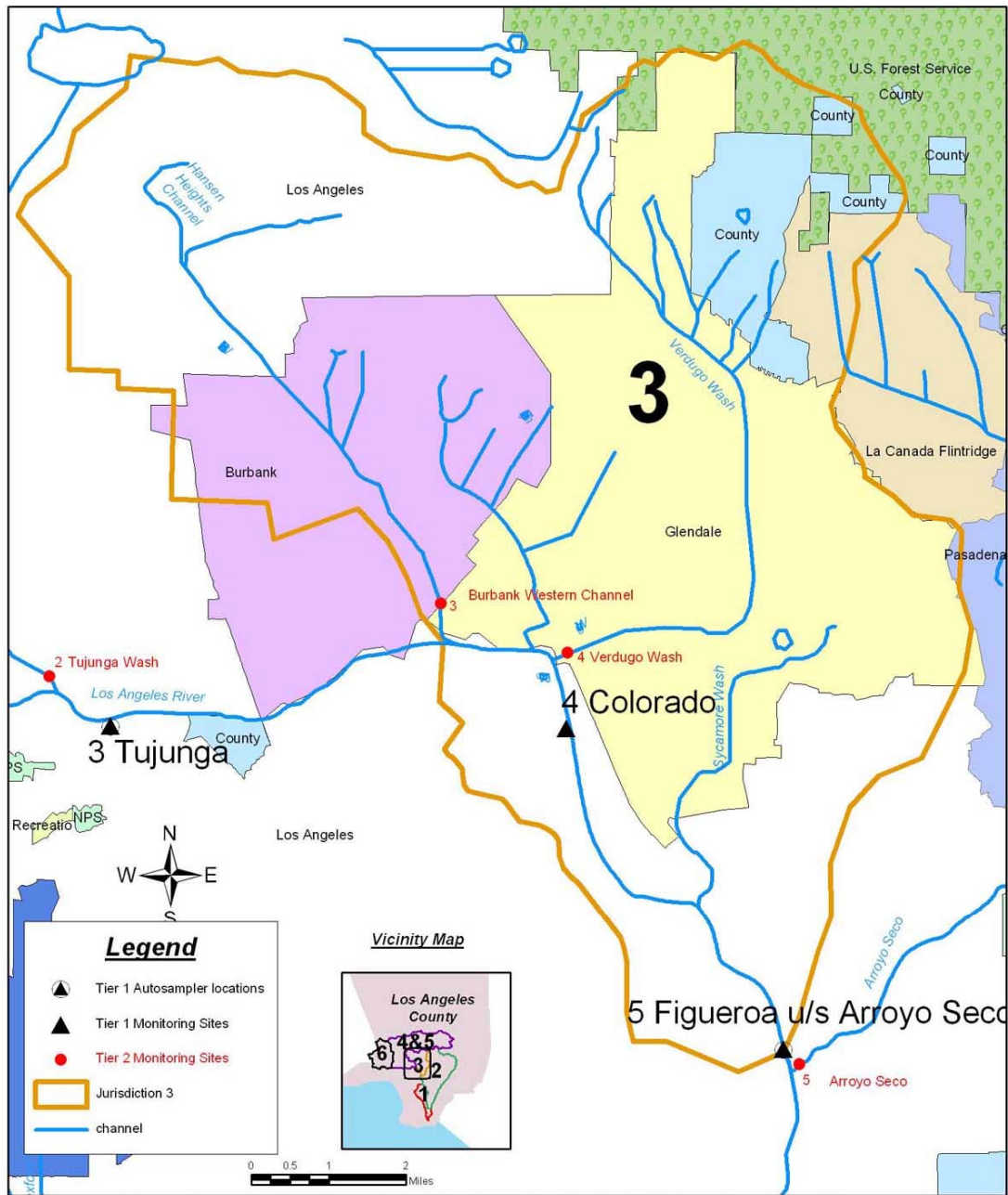
Los Angeles River Metals TMDL Jurisdiction 1 Cities Map

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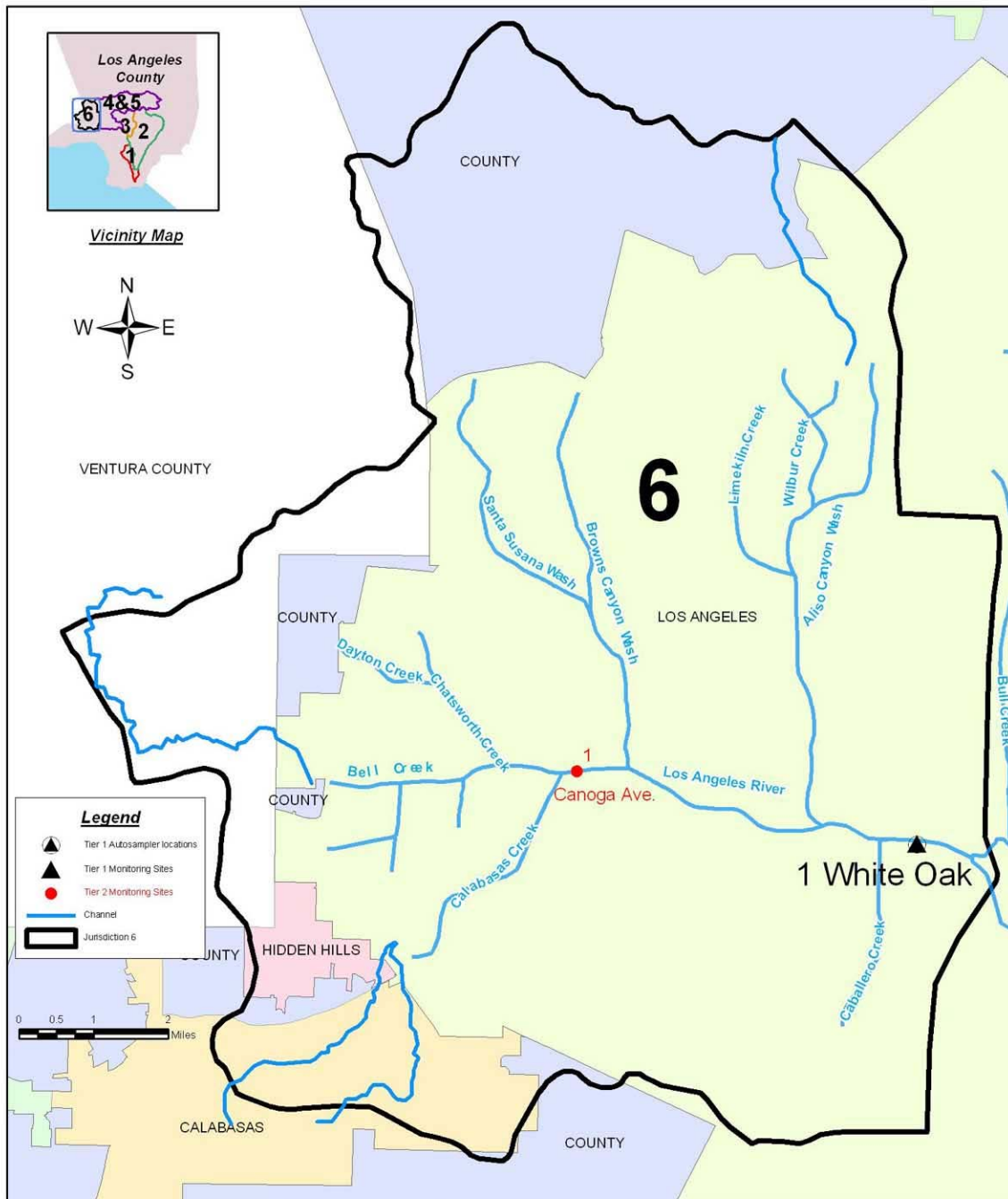
Los Angeles River Metals TMDL Jurisdiction 2 Cities Map

<div> SANITATION DEPARTMENT OF PUBLIC WORKS</div>	RITA L. ROBINSON DIRECTOR		DEPARTMENT OF PUBLIC WORKS		SHAHRAM KHARAGHANI PROGRAM MANAGER		<div> WATERSHED PROTECTION CITY OF LOS ANGELES</div>
	FILE-LOC F:/LARTMDL/Metals TMDL GIS	DRAWN BY: SC	CHECKED BY: PW	DATE 11/07/06 DATE REVISED 11/07/06	This map shall not be copied or reproduced, all or any part thereof, whether for distribution or resale, without the proper written permission of the Dept. of Public Works, City of Los Angeles Thomas Bros Data reproduced with permission granted by THOMAS BROS MAP		





CITY OF LOS ANGELES SANITATION DEPARTMENT OF PUBLIC WORKS	RITA L. ROBINSON DIRECTOR		DEPARTMENT OF PUBLIC WORKS		SHAHRAM KHARAGHANI PROGRAM MANAGER	 WATERSHED PROTECTION CITY OF LOS ANGELES
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Los Angeles River Metals TMDL Jurisdiction 6 Cities Map

<p>CITY OF LOS ANGELES</p>  <p>SANITATION DEPARTMENT OF PUBLIC WORKS</p>	<p>RITA L. ROBINSON DIRECTOR</p> <p>FILE-LOC F:\ARTMDL\Metals TMDL GIS</p>	<p>DEPARTMENT OF PUBLIC WORKS</p> <p>DRAWN BY: SC</p> <p>CHECKED BY: PW</p>	<p>SHAHRAM KHARAGHANI PROGRAM MANAGER</p> <p>DATE 11/07/06</p> <p>DATE REVISED 11/07/06</p>	<p>This map shall not be copied or reproduced, all or any part thereof, whether for distribution or resale, without the proper written permission of the Dept. of Public Works, City of Los Angeles Thomas Bros Data reproduced with permission granted by THOMAS BROS MAP</p>	 <p>WATERSHED PROTECTION CITY OF LOS ANGELES</p>
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APPENDIX D

Collection and Sampling Standard Operating Procedures

General Safety

- A. Be Alert: Always be aware of potentially hazardous situations. Exercise common sense when you encounter suspicious persons or animals. Your personal safety is your first responsibility. Never place yourself in a dangerous or unsafe situation.
- B. Traffic: Always be mindful of traffic conditions. Always wear high-visibility clothing (ANSI 107 Class 2) when sampling near areas open to vehicular traffic. Never sample in traffic conditions that you feel are unsafe. Never attempt to setup a traffic-stop without the proper equipment and training.
- C. Always wear protective gloves and eyewear when collecting water samples. Avoid water contact with eyes and skin. If accidental contact with eyes occurs, use portable eyewash bottles as directed. Wash hands thoroughly after collecting samples.
- D. Always wear chemical-resistant, slip-resistant shoes when collecting samples.
- E. Never enter the flood channel when there is high flow or during rainy conditions. Never stand or walk in moving water. Never get too close to the low-flow channel.
- F. Never enter an enclosed drain, tunnel, or confined space. These spaces can become devoid of oxygen/air and you can suffocate.
- G. Never sample alone. At least two people must be present at all times. Take communication equipment (cell phones) with you to report any accidents, seek assistance, or maintain contact with your partner.

Dry Weather Water Quality Sampling

Sampling Procedure

A. Coordination with Laboratory.

At the beginning of each month, the monthly sampling schedule is sent via email to the supervisors of the participating laboratories. If unforeseen changes are made to the schedule, the labs should be notified immediately. Contact information is listed at the end of this appendix.

B. Gather the necessary equipment

1. First Aid kit
2. Portable eyewash bottle with saline solution
3. Ice chest (with ice)
4. Sampling pole with reel
5. Weighted bottle holder (attaches to fishing line/reel)
6. Nalgene 1-liter sample bottles, acid-washed
7. Nalgene 500-mL sample bottles, acid-washed (for sampling low-flow streams)
8. Wash bottle with de-ionized water
9. Foaming disinfectant hand cleanser
10. Waterproof labels
11. Paper towels
12. Water-safe pen and Lab marker
13. Field log sheet
14. Chain-of-Custody (COC) sheet
15. Thomas Guide (street map)
16. Trash bag
17. Cell phones (1 for each person)
18. Personal protective equipment:
 - i. Safety vest (ANSI 107 Class 2 compliant, high visibility)
 - ii. Protective gloves (latex, nitrile, etc.)
 - iii. Slip-resistant shoes/boots
 - iv. Protective eyewear: UV protection; impact resistant
 - v. Foul weather gear (when necessary)
 - vi. Rain boots (when necessary)
 - vii. Life vest (if entering the flood channel).

C. Sampling Locations

Tier I and Tier II sampling stations are listed in the table below. Prior to sampling, confirm which stations are to be sampled (Tier I vs. Tier II).

Station ID			Waterbody	Location	Thomas Guide Coordinates
Tier I	JUR. 1	LAR1-9	Main Channel	@ Wardlow Ave	765 - C7
	JUR. 2	LAR1-6	Main channel	@ Washington	674 - J1
		LAR1-7	Main Channel	@ U/S Rio Hondo	705 - F6
		LAR1-8	Main Channel	@ Del Amo Blvd	765 - C4
	JUR. 3	LAR1-4	Main Channel	@ Colorado	564 - C5
		LAR1-5	Main Channel	@ Figueroa upstream of Arroyo Seco	594 - H7
	JUR. 4 & 5	LAR1-2	Main Channel	@ Sepulveda	561 - H3
		LAR1-3	Main Channel	@ Tujunga	652 - J6
	JUR. 6	LAR1-1	Main Channel	@ White Oak	531 - B7
Tier II	JUR. 1	LAR2-7	Compton Creek	@ Del Amo Blvd	765 - B4
	JUR. 2	LAR2-5	Arroyo Seco	@ San Fernando Rd.	594 - F2
		LAR2-6	Rio Hondo	@ Garfield Ave	705 - G5
	JUR. 3	LAR2-3	Burbank Western Channel	@ Riverside Dr	562 - J3
		LAR2-4	Verdugo Wash	@ Concord St	564 - C3
	JUR. 4 & 5	LAR2-2	Tujunga Wash	@ Moorpark Ave	562 - G4
	JUR. 6	LAR2-1	Main Channel D/S Confluence	@ Canoga Park	530 - B6

D. QA&QC

a. Field Log sheet

A field log sheet is provided in Appendix 2. This form is for recording details about each sampling event (including Date, time, locations, samplers, comments), and is retained by the sampling staff. The form is to be prepared before leaving to the field, and the appropriate information is filled out after each sample is collected.

b. Chain of Custody (COC) form

A COC form is to be completed for each sampling event. The form should be prepared prior to leaving to the field. At each sampling station, the sampler enters his/her initials, along with time of collection. The original COC is to follow the samples at all times. The sampler must sign and date the COC when relinquishing the sample to Laboratory Staff (Sample Receiving, EMD) who in turn, signs the form to indicate receipt of the sample. A photocopy is given to the sampling staff, and the laboratory retains the original COC along with the samples to be analyzed. A sample of a COC form is provided in Appendix F.

c. Collecting Samples

When sampling from a bridge, a fishing pole/reel is used to lower the sample bottle into the stream.

- (1) Obtain a clean, acid-washed bottle (1Liter, plastic nalgene). Confirm that the bottle has the appropriate pre-printed label. If the depth of the water is low, it may be necessary to collect multiple samples using a smaller bottle (500 mL), and compositing sub-samples until a volume of 1 Liter is obtained.
- (2) Note the sample collection time on the Field Log sheet, COC, and sample label.
- (3) Be very careful to avoid contamination of the sample bottle. Avoid touching the mouth of the bottle and the inside of the cap.
- (4) Attach the bottle-holder to the fishing line, and secure the bottle. Unscrew the bottle lid, and set it aside. Release the drag on the reel, and lower the bottle into the stream. Allow the bottle to fill with water, and then reel it in. Replace the lid securely, and place the sample into the ice chest.
- (5) Rinse bottle holder with de-ionized water after each station.
- (6) Fill in appropriate information on the COC and field log sheet.
- (7) Samples should be delivered to the laboratory as soon as possible. When relinquishing custody of the samples, inform Laboratory staff that samples need to have preservative added (this should also be indicated on the COC). Sign and date the COC, and obtain a copy after the laboratory staff member has signed the original.
- (8) Upon returning from the field, file the COC (copy) and field log sheet in the appropriate binder. Rinse all field equipment with de-ionized water.

Wet Weather Water Quality Sampling

Sampling Procedure

A. Wet weather water sampling

- a. Flow-weighted composite samples will be collected to obtain the representative sample for each storm event. This sampling method is currently used for the storm water monitoring required by Los Angeles County's NPDES permit. A flow-weighted composite sample is obtained by mixing a series of discrete samples (aliquots) of specific volume, collected at specific runoff volume intervals over the duration of the storm event. The concentration of the sample is called Event Mean Concentration (EMC).
- b. An automatic sampler will be programmed to start automatically when the water level in the channel or storm drain exceeded a certain height such that the corresponding flow rate exceeded a pre-determined wet weather flow rate at the sampling location. Samples will be retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall and runoff data were logged and stored for transfer to the office. The automated sampler will be programmed with the intent of capturing the major portion of a runoff event

B. Wet weather water data per metals TMDL

The metals load at each monitoring site will be estimated by multiplying the EMC by the total runoff volume measured at the site. The total runoff volume can be calculated based on the runoff hydrograph that would be generated over the entire storm duration by the continuous measurements of flow rate by the automatic samplers. Similarly, the daily metal load can be calculated by multiplying the daily runoff volume by the EMC

C. QA&QC

- a. Sampling methodology
Properly performed monitoring station set up, water sample collection, sample transport, and laboratory analyses are vital to the collection of accurate data. Quality Assurance/Quality Control (QA/QC) is an essential component of the monitoring program. *Evaluation of Analytes and QA/QC Specifications for Monitoring Program* (Woodward-Clyde 1996a) and *Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to West Coast Marine and Estuarine Organisms* (USEPA 1995) describe the procedures used for bottle labeling, chain-of-custody tracking, sampler equipment checkout and setup, sample collection,

field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory. An important part of the QA/QC Plan is the continued education of all field personnel. Field personnel will be adequately trained from the onset and informed about new information on storm water sampling techniques on a continuing basis. Field personnel also evaluate the field activities required by the QA/QC Plan, and the Plan is updated if necessary.

b. Bottle Preparation.

(1) For each monitoring station, a minimum of three sets of bottles will be available so that up to two complete bottle change-outs could be made for each storm event. Bottle labels contained the following information

- (i) Sample ID Number
- (ii) Station Number
- (iii) Station Name
- (iv) Sample Type (Grab or Composite)
- (v) Laboratory Analysis Requested
- (vi) Date
- (vii) Time
- (viii) Preservative
- (ix) Temperature
- (x) Sampler's Name

(2) Bottles will be cleaned at the laboratory prior to use, and then they will be labeled and stored in sets. Each station will be provided with the same number, types, and volumes of bottles for each rotation. Clean composite sample bottles will be placed in the automated sampler when samples are collected. This practice ensures readiness for the next storm event. All bottles currently not in use are stored and later transported in plastic ice chests. Composite sample bottles are limited to a maximum of 2.5 gallons each, to ensure ease of handling.

c. Chain-of-Custody Procedure

Chain-of-Custody forms will be completed to ensure and document sample integrity. These procedures establish a written record which tracks sample possession from collection through analysis.

d. Field Setup Procedures

(1) All field-sampling locations will be fixed sites, with the automated sampler placed on a public road or flood control right-of-way. After sample collection, field staff will prepare the sampler for collection of the next set of samples. Inspection of visible hoses and cables will be performed to ensure proper working conditions according to the site design. Inspection of the automatic sampler and appurtenances including strainer, pressure transducer, and auxiliary pump will be performed during daylight hours in non-storm conditions. The automated sampler will be checked at the beginning of the storm to ensure

proper working condition and to see if flow composite samples are being collected properly.

- (2) Bottles will be collected after each event and packed with ice and foam insulation inside individually marked ice chests. Chain-of-Custody forms will be completed by field staff before transportation of the samples to the laboratory. Under no circumstance will the samples be removed from the ice chest during transport from the field to the laboratory.

e. Travel Blanks and Field Duplicates

Potential field contamination will be assessed through analysis of travel blanks and duplicate grab samples. Field travel blanks will be collected for each monitoring station during every sampling event to quantify post-sampling contamination. The monitoring program also includes field duplicates to assess the precision of laboratory results. A field duplicate, the origin of which is unknown to the laboratory, will be collected for each sampling event. This methodology for assessing post-sampling contamination and laboratory testing procedures provided data to measure the precision and accuracy of the laboratory results

Contact Information: Jeff Beller to the lab contact list (Assistant Division Manager). 310-648-5262.

Laboratory:

Data/Sample Management

- Supervisor: Susan Chang
Phone: (310) 648-5607
Email susan.chang@lacity.org
- Sample Receiving Desk
Phone: (310) 648-5831

Inorganic Laboratory (Metals)

- Supervisor: Soun Chanjamsri
Phone: (310) 648-5995
Email soun.chanjamsri@lacity.org

Assistant Division Manager

- Supervisor: Jeffrey Beller
Phone: (310) 648-5262
Email: jeffrey.beller@lacity.org

Recipients of lab results:

Watershed Protection Division:

- Pollution Assessment Section
Supervisor: Vivian Marquez
Phone: (323) 342-1556
Email vivian.marquez@lacity.org
- TMDL Implementation Section
Supervisor: Morad Sedrak
Phone: (213) 485-3951
Email morad.sedrak@lacity.org

APPENDIX E

Safety

Field Sampling Safety

For employees who have been assigned the duty of sample collection, there must be an awareness of the potential hazards involved at both the site and in the sampling subject. The following are general precautions to be observed during sample collection.

- a. Use proper equipment for the job. This includes personal protective gear such as eye protection, gloves, boots, or hardhat, when necessary; and equipment required to aid in sampling such as poles and holders for the bottles.
- b. No Laboratory Technician should sample alone prior to proper training; if possible bring someone along to assist.
- c. Be sure samples are secure in the vehicle or mode of transport to avoid the risk of contamination and the possibility of spillage resulting in exposure.
- d. Never deliberately touch the water or waste being sampled. Remember that these substances could pose a risk to your health.
- e. Disinfect hands and exposed body parts after sampling, and be sure to clean off utensils, gloves, and boots to protect others.

During sampling, safety of the sampler is of prime importance. If a sample location is inaccessible or deemed to be unsafe, no sample is required to be collected and comments should be noted on the observation sheet. During wet weather, safety consideration may preclude collection of a sample.

Laboratory Safety

The collection and analysis of environmental samples involves contact with samples that may contain agents that pose a microbiological and/or chemical hazard. The primary means of exposure to these microbiological hazards involve body contact during sample collection and hand-mouth or nose contact while handling the samples. Personal protective measures are mandatory while working in the field and laboratory. Following are some key steps to be followed by all laboratory analysts:

- a. Assure that appropriate eye protection is worn by all persons, when toxic materials (chemicals or biochemicals) are handled. Contact lenses should not be worn when working with chemicals.

- b. Wear appropriate gloves when the potential for contact with toxic materials exists; inspect gloves before each use, wash them before removal, and replace them periodically.
- c. Persons doing sampling must wear boots. The boots must be cleaned before entering the building. Boots cannot be worn in the lunchroom, under any circumstances. Steel-toed chemical resistant boots should be worn for the harshest environments, where there is also risk of injury to the foot and toes.
- d. Use any other protective and emergency apparel and equipment as appropriate.
- e. Remove laboratory coats immediately when exposed to significant contamination.

The following guidelines are designed to prevent any exposure of personnel to hazardous agents.

- 1. Hazardous areas and receptacles of contaminated items are to be properly labeled.
- 2. Never pipette by mouth. Use bulbs or other mechanical means to draw up the liquid.
- 3. Safety cabinets of the appropriate type and class are to be supplied, maintained, and used.
- 4. Employees should use the provided bottle carriers when moving reagents, acids, and solvents through the building.
- 5. Laboratory personnel must follow labeling protocols in the laboratory to prevent mix-ups of reagents, and when possible use the pre-labeled or permanently labeled bottles. Secondary containers are to be labeled as well.

APPENDIX F

Chain-of-Custody Form

Examples of worksheets for Chain of Custody sheets (next 2 pages) used by the City of Los Angeles' Environmental Monitoring Division are provided herein.

This part left intentionally Blank

Date: _____



Department of Public Works
Bureau of Sanitation
Environmental Monitoring Division

Sample Chain of Custody

EMD
LIMS #: _____

EMD Sample ID: _____
Project Name: _____

Sampling Information:	
Sampling Agency: _____	Sampling Program: _____
Agency Sample ID#: _____	_____
Phone Number: _____	_____
Fax Number: _____	Purpose of program: _____
Contact Person: _____	_____
email address: _____	Report Time Frame: _____
_____	_____
Sampler's Name: _____	_____
Sampler's Title _____	_____
Sampler's Signature: _____	_____
Witness: Name _____	Sample Date: _____
Title _____	_____
Name _____	Sampling Time: _____
Title _____	_____
Sample Location: _____	Sampling Address: _____
_____	_____
_____	_____

Requested Analysis:	Metals: <input type="checkbox"/>	Micro Biological: <input type="checkbox"/>
	Organics: <input type="checkbox"/>	Toxicity: <input type="checkbox"/>
	Conventional Chemistry: <input type="checkbox"/>	Air Testing: <input type="checkbox"/>
	See back of page for specifics analyses	

Sample Notification:

PC: _____	Date: _____	Toxicity: _____	Date: _____
Wet: _____	Date: _____	Metals: _____	Date: _____
Micro: _____	Date: _____	Semi-Vol: _____	Date: _____
		Volatile: _____	Date: _____

Current Holder Name	Signature	Title	Received Date	Received Time	Released Date

Analysis to be performed on the Sample(s):

EMD

LIMS #:

Locator:	Collection Time:	Locator:	Collection Time:
-1 _____	_____	-6 _____	_____
-2 _____	_____	-7 _____	_____
-3 _____	_____	-8 _____	_____
-4 _____	_____	-9 _____	_____
-5 _____	_____	-10 _____	_____

Sample Information:	Liquid: <input type="checkbox"/>	Solid: <input type="checkbox"/>	Other: <input type="checkbox"/>	Temperature _____
Grab <input type="checkbox"/>	Composite: <input type="checkbox"/>	Start time: _____		Finish time: _____
Container:	Glass	Size: _____	Color: _____	Number: _____
	Plastic	Size: _____	Color: _____	Number: _____
Preservative <input type="checkbox"/>	Number of samples: <input type="text"/>			Residual Cl2 _____
				pH _____

Metals:

<input type="checkbox"/> Ag	<input type="checkbox"/> Cu	<input type="checkbox"/> Pb	<input type="checkbox"/> Other: _____
<input type="checkbox"/> Al	<input type="checkbox"/> Fe	<input type="checkbox"/> Sb	
<input type="checkbox"/> As	<input type="checkbox"/> Hg	<input type="checkbox"/> Se	
<input type="checkbox"/> Ba	<input type="checkbox"/> K	<input type="checkbox"/> Sn	
<input type="checkbox"/> Be	<input type="checkbox"/> Mg	<input type="checkbox"/> Sr	<input type="checkbox"/> Total
85 <input type="checkbox"/> Ca	<input type="checkbox"/> Mn	<input type="checkbox"/> Tl	<input type="checkbox"/> Dissolved
<input type="checkbox"/> Cd	<input type="checkbox"/> Mo	<input type="checkbox"/> V	
<input type="checkbox"/> Co	<input type="checkbox"/> Na	<input type="checkbox"/> Zn	
<input type="checkbox"/> Cr	<input type="checkbox"/> Ni		

Organics:	<input type="checkbox"/> VOC	<input type="checkbox"/> Pesticides/PCB	<input type="checkbox"/> Clopyralid	<input type="checkbox"/> Air VOC
	<input type="checkbox"/> BNA	<input type="checkbox"/> Dioxin - screen	<input type="checkbox"/> Dioxin - low resolution	<input type="checkbox"/> Fixed Gases
	<input type="checkbox"/> TOX	<input type="checkbox"/> Other: _____	<input type="checkbox"/> Dioxin - high resolution	<input type="checkbox"/> GC Sulfur
	<input type="checkbox"/> Herbicides		<input type="checkbox"/> Tributyltin	<input type="checkbox"/> Siloxanes

Conventional Chemical:

<input type="checkbox"/> Alkalinity	<input type="checkbox"/> MBAS	<input type="checkbox"/> Solids:
<input type="checkbox"/> BOD	<input type="checkbox"/> Nitrogen:	<input type="checkbox"/> Total Solids
<input type="checkbox"/> Boron	<input type="checkbox"/> Ammonia Nitrogen	<input type="checkbox"/> Total Dissolved Solids
<input type="checkbox"/> Chloride	<input type="checkbox"/> Nitrate-N	<input type="checkbox"/> Total Suspended Solids
<input type="checkbox"/> COD	<input type="checkbox"/> Nitrite-N	<input type="checkbox"/> Settleable Solids
<input type="checkbox"/> Conductivity	<input type="checkbox"/> Organic-N	<input type="checkbox"/> Volatile Suspended Solids
<input type="checkbox"/> Cyanide (Free)	<input type="checkbox"/> Kjeldahl Nitrogen	<input type="checkbox"/> Volatile Total Solids
<input type="checkbox"/> Cyanide (Total)	<input type="checkbox"/> Oil & Grease	<input type="checkbox"/> Sulfates
<input type="checkbox"/> Flashpoint	<input type="checkbox"/> pH	<input type="checkbox"/> Sulfides, Total
<input type="checkbox"/> Fluoride	<input type="checkbox"/> Phenols	<input type="checkbox"/> Sulfides, Dissolved
<input type="checkbox"/> Grain Size	<input type="checkbox"/> Phosphate, Total	<input type="checkbox"/> Thiosulfate
<input type="checkbox"/> Hardness	<input type="checkbox"/> Phosphate, Dissolved	<input type="checkbox"/> TOC
<input type="checkbox"/> Hexavalent Chromium	<input type="checkbox"/> Radioactivity	<input type="checkbox"/> Turbidity
<input type="checkbox"/> H ₂ S	<input type="checkbox"/> Salinity	<input type="checkbox"/> Other: _____

Biological:

<input type="checkbox"/> Total Coliform	<input type="checkbox"/> Salmonella	<input type="checkbox"/> Other: _____
<input type="checkbox"/> Fecal Coliform	<input type="checkbox"/> Acute Toxicity (Fresh water)	_____
<input type="checkbox"/> E. coli	<input type="checkbox"/> Chronic Toxicity (Sea water)	_____
<input type="checkbox"/> Enterococcus	<input type="checkbox"/> Chronic Toxicity (Fresh water)	

Remarks: _____

APPENDIX G

Laboratory Standard Operating Procedures (City of Los Angeles)

WATER QUALITY MONITORING STANDARD OPERATING PROCEDURES

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ENVIRONMENTAL MONITORING DIVISION
Hyperion Treatment Plant - Instrumental Chemistry Strategic Business Unit
– Metals Laboratory

**STANDARD OPERATING PROCEDURE for INDUCTIVELY
COUPLED PLASMA-ATOMIC EMISSION
SPECTROMETRIC METHOD FOR TRACE ELEMENT
ANALYSIS OF WATER AND WASTES**

(EPA Methods 200.7)

EMD SOP# 6200.7

Effective Date: 03/01/03

Version No.: 1

Total Number of pages: 11

Prepared by: Magdi Hanna

Pages Revised

APPROVAL:

Laboratory Manager: Lee Huang

Signature:

Quality Assurance Manager: Jeff Beller

Signature:

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1. Scope and Application

This method may be used for the determination of dissolved, suspended, or total elements in drinking water, surface water, and domestic and industrial wastewaters. It is based primarily on EPA method 200.7, 6010B and also on SM3120. User of this SOP should be familiar with those methods and also with the EPA digestion method 30005, 3010A, 3020A, 3050B and the SM3030 series.

Dissolved elements are determined in filtered and acidified samples. Appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 mg/L.

Total elements are determined after appropriate digestion procedures are performed. Since digestion techniques increase the dissolved solids content of the samples, appropriate steps must be taken to correct for potential interference effects.

Table 1 lists elements for which this method applies along with recommended wavelengths and typical estimated instrumental detection limits using conventional pneumatic nebulization. Actual working detection limits are sample dependent and as the sample matrix varies, these concentrations may also vary.

2. Summary of Method

The method describes a technique for the simultaneous multi-element determination of trace elements in solution. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency (RF) inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photosensitive device. The photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements.

3. Interferences

Several types of interference effects may contribute to inaccuracies in the determination of trace elements. They can be summarized as follows:

Spectral interferences can be categorized as (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) background contribution from stray light from the line emission of high

concentration elements. Utilizing a computer correction of the raw data, requiring the monitoring and measurement of the interfering element can compensate the first of these effects. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line.

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples, which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may lessen these interferences.

Molecular compound formation, ionization effects and solute vaporization effects characterize chemical Interferences. Normally these effects are not pronounced with the ICP technique, however, if observed they can be minimized by careful selection of operating conditions, by buffering of the sample, by matrix matching, and by standard addition procedures.

4. Sample Handling and Preservation

For the determination of trace elements, contamination and loss are of prime concern. Dust in the laboratory environment, impurities in reagents and impurities on laboratory apparatus, which the sample contacts are all sources of potential contamination. Sample containers can introduce either positive or negative errors in the measurement of trace elements by (a) contributing contaminants through leaching or surface desorption and (b) by depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis requires particular attention.

Before collection of the sample a decision must be made as to the type of data desired, that is dissolved, suspended or total, so that the appropriate preservation and pretreatment steps may be accomplished. Filtration, acid preservation, etc., are to be performed at the time the sample is collected or as soon as possible thereafter. If properly acid preserved ($\text{pH} < 2$), the sample can be stored up to 6 months before analysis.

For the determination of dissolved elements the sample must be filtered through a 0.45 μm pore-size membrane filter as soon as practical after collection. Acidify the filtrate with (1 + 1) HNO_3 , to a pH of 2 or less.

For the determination of suspended elements a measured volume of unpreserved sample must be filtered through a 0.45 μm pore-size membrane filter as soon as practical after collection. The filter plus suspended material should be transferred to a suitable container for storage and/or shipment. No preservative is required.

For the determination of total or total recoverable elements, the sample is acidified with (1+1) HNO₃, to pH 2 or less as soon as possible, preferably at the time of collection. The sample is not filtered before processing. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH <2 before analysis. If pH is still high, the pH should be adjusted again, held for sixteen hours, and re-checked until verified to be pH<2 before analysis. Solid sample only require to be stored at 4°C.

5. Apparatus

Inductively Coupled Plasma-Atomic Emission Spectrometer (Varian Vista-Pro)

Compaq Deskpro Personal Computer, Varian cooler/recirculator

Argon gas supply- high purity grade or better.

The ICP-AES used at EMD lab at HTP is a Varian vista-pro Analytical Instruments model Vista CCD ICP_OES. It is a simultaneous, multi-elementals analyzer with an axially viewed plasma, a purged Echelle polychromator and a solid state charged coupled device (CCD) detector with excess capacity to allow for simultaneous multi-frequencies, multi-elements analyses. It is capable of high spectral resolution even in the UV region therefore minimizing spectral interferences while increasing sensitivity of emission line detection. This SOP must be used in conjunction with the operating manual for the Varian vista-pro. The Vista-pro is computer control for plasma alignment and ignition. Its software includes the FACT (Fast Automated Curve-fitting Technique) inter-elements correction routine for spectral and background correction. This routine used spectral information of potential interfering elements, stored in its memory to synthesize a matching spectral contour adjacent to the peak of analyte of interest in the sample and subtract that from the apparent sample's spectrum to obtain the corrected spectrum. The software also contains library of all potential atomic spectral interference lines for all elements, so user can easily choose the emission line with the minimum potential for atomic spectral interference. The vista-pro is also equipped with an automatic sampler with a peristaltic pump to minimize physical interference in the sample transporting system.

6. Reagents and Standards

1. Acids used in the preparation of standards and for sample processing must be trace metals high purity grade or equivalent.

Hydrochloric acid-Conc. (sp gr 1.19)

Nitric acid-Conc. (sp gr 1.41).

2 Deionized, Distilled Water-Prepared by passing distilled water through a mixed bed of cation and anion exchange resins. Deionized, distilled water is used for the preparation of all reagents, calibration standards and as dilution

water. The purity of this water must be equivalent to ASTM Type II reagent water of Specification.

3. Standard stock solutions may be purchased or prepared from ultra high purity grade chemicals. Single element stock solutions of 1000 mg/L, used here, were purchased from SPEX and from Environmental Resource Associate.

4. Mixed Calibration Standard Solutions- stock of the mixed calibration were purchased from Inorganic Ventures Inc., Ultra Scientific and from SPEX. These stocks included:

WW-IPC-1 (1000 mg/L each P, K; 200 mg/L each Al, As, Ba, Be, B, Cd, Ca, Ce, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Ni, Se, Na, Sr, Ti, V, Zn; 25 mg/L Ag)

WW-IPC-2 (1000 mg/L SiO₂, 200 mg/L each Sb, Mo, Sn, Ti)

ICM-240 (100 mg/L each P, K, Si; 20 mg/L each Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Ti, Sn, V, Zn; 5 mg/L Ag)

ICM-245 (50 mg/L P, 25 mg/L each Al, Sb, As, Ba, B, Cr, Cu, Fe, Pb, Li, Mn, Ni, Se, Si, Sr, Ti, Zn, 10 mg/L each Cd, Co, Mn, Sn, V, 5 mg/L each Be, Hg, 2.5 mg/L Ag)

LPC Standard 1 (constituents and concentration the same as ICM-240)

LPC Standard 2 (same as ICM-245) etc.

The working mixed calibration standards were prepared by combining appropriated volumes of the stock standard solutions in volumetric flasks. The following working mixed calibration standard are used:

Std#1 (ML Be, Pb)=0.002 mg/L Be, and 0.005 mg/L Pb, from a mixture of the single stocks of Be and Pb.

Std#2 (ML 0.01)=0.01 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Ti, Sn, V, Zn, 0.05 mg/L each of K, SiO₂ and 0.00125 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2. Omit Ag at this low concentration in the actual calibration.

Std#3 (ML Ag)=0.08 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Ti, Sn, V, Zn; 0.40 each of K, SiO₂ and 0.01 of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

Std#4 (1.0 mg/L)=1.0 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Ti, Sn, V, Zn; 5.0 mg/L each of K, SiO₂ and 0.125 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

Std#5 (4.0 mg/L)=4.0 mg/L each of Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Mo, Ni, Se, Na, Sr, Ti, Sn, V, Zn; 20 mg/L each of K, SiO₂ and 0.50 mg/L of Ag from a serial dilution of the mixture of equal volume of WW-IPC-1 and WW-IPC-2.

It should be noted that if the analysis of the metal components contained in WW-IPC-2 are not required (i.e., do not need Sb, Mo, SiO₂ and Sn) then only the stock of WW-IPC-1 should be used in the preparation of Std#2 to Std#5. Further more since the method requires only blank and three others calibration standards for the calibration of the instrument, the analyst has the option not to

include one or two of the ML mixed calibration standards (if this exclusion still meet the ML requirements of the regional water quality control board for the permit reporting) in the actual calibration.

Std#6 (20.0 mg/L)= 20.0 mg/L each of Al, Na, Fe, K, Ca, Mg from the single stocks of 1000 mg/L of Al, Na, Fe, K and Ca.

Std#7 (40.0 mg/L)= 40.0 mg/L each of Al, Na, Fe, K, Ca, Mg from the single stocks of 1000 mg/L of Al, Na, Fe, K and Ca.

Std#6 and 7 are included here only if the analyst want to extend the upper linear dynamic range of those elements by monitoring of the lower sensitive wavelengths of those elements.

The mixed standard solutions are transferred to a polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample.

The acceptable correlation coefficient of linearity for the calibration of each frequency must be 0.998 or greater.

5. Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve while the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

The calibration blank is prepared by diluting 10 ml of conc. HNO₃ to 1000 ml with deionized, distilled water.

The reagent blank must contain all the reagents and in the same volumes as used

in the processing of the samples. The reagent blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

6. Instrument performance check (IPC) solution is prepared by the analyst using mixture of WW-IPC-1+2. The IPC solution is used to periodically verify instrument performance or drift during analysis. It should be prepared in the same acid mixture and same source as calibration standards. Silver must be limited to <0.5 ppm while potassium and silica should be at 10 ppm. For all other analytes a concentration of 2 ppm is recommended. Analysis of the IPC solution immediately following calibration must verify that the observed values are within 5% of the expected values. Subsequent analyses of the IPC solution must be within 10% limit. Analyze the IPC solution following each 10 samples and at the end of the run. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed.

7. Spectral interference check (SIC) solution: Prepared by the analyst, using a mixture of IPC 1+2 2.0 ppm conc. Spiked with 100 ppm of the single analytes Al, Fe, Na, K, Ca, Mg. This solution is to verify the FACT feature used to separate

the interferer peaks from the interference analytes, should confirm an operative interference that is 10% range of the analyte conc.

8. The quality control sample (QCS): Must be obtained from an outside source different from the standard stock solutions used for the preparation of the calibration standards and should be prepared in the same acid matrix as the calibration standards at a concentration $>$ or $=$ 1 mg/L, except for silver, which must be limited to a concentration of 0.5 mg/l (in our case ICM-240 is used from ULTRA SCIENTIFIC with the proper dilution).

9. Laboratory fortified sample matrix (LFM) and its duplicate: Prepare by adding 1.0 ml of ICM240 stock into an aliquot of the sample (100 ml for surface, ground water, treatment plant effluents and 50 ml for industrial waste samples).

10. Laboratory fortified blank (LFB): Prepare by adding 1 ml of ICM240 stock into calibration blank and make up volume to 100 ml. It must be treated the same as sample in a batch (must gone thru the same sample preparation steps).

7. Safety

The toxicity and carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis.

Safety goggle and protective lab coat must be worn all the time while working in the lab. Wear glove when handle samples and chemicals.

8. Procedure

Sample Preparation: Refer to (EPA method 3005, 3010A, 3020A and SM3030) SOP on sample preparation.

Instrument start-up and warm-up procedures:

- 1. Open the Argon supply, turn on the cooling system, attach the tubing in the peristaltic pump.**
- 2. In the main menu of the ICP program, set “instrument parameters” to:**
Coolant flow = 12-13 ml/min
Auxiliary flow =1.5ml/min,
Nebulizer flow = 0.9ml/min

4. Turn on the pump and the hood the moment the plasma is lighted. The instrument is allowed to stabilize for at least 30 minutes before analysis is started.
5. Reprofile optics and optimize the torch position before actual analysis is done once a month as recommended by the manufacture.

Sample Analysis

1. Choose and update the method and prepare the standards and samples sequence.
2. Calibrate the instrument then analyze the samples.
3. Analyze calibration blank, Instrument Performance Check , Spectral interference check at the frequency specified in the method (see section 11).

9. Calculation

Reagent blanks (Section 6.5) should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions were performed, the appropriate factor must be applied to sample values.

Data should be rounded to the thousandth place and all results should be reported in mg/L up to three significant figures.

10. Data Management

Raw data are stored in ICP software under the filename "E:\ICP\2003\yymmdd.CSV". For data reduction, the same data are extracted and transferred to "EMDB/ICP_DATA/2003". Final results are manually entered into Laboratory Information Management System. A hard copy of all the raw data is kept in the laboratory for five years.

11. Quality Control

The initial demonstration of performance for this method consists of conducting Linear Dynamic Range (LDR), QCS, and Method Detection Limit (MDL). The first two requirements are discussed below.

Check the instrument standardization and method performance by analyzing appropriate quality control check standards as follow:

Instrument performance check standard (IPC) containing the elements of interest are analyzed immediately following a blank, after the calibration, and at a frequency of 10% thereafter. This check standard is used to determine instrument drift. If agreement is not within 5% initially and 10% subsequently of the expected values the analysis is out of control. The analysis should be terminated, the problem corrected, and the instrument recalibrated.

Laboratory reagent blank (LRB) The laboratory must analyze at least one LRB with each batch of 20 or fewer samples of the same matrix. When LRB values constitute 10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again after the source of contamination has been corrected and acceptable LRB values have been obtained.

Spectral interference check (SIC) is analyzed at the beginning, end, and at periodic intervals throughout the sample run to verify interelement and background correction factors. Results should fall within the established control limits of one and a half times the standard deviation of the mean value. If the results are not within the control limit, the analysis is terminated, the source of the problem identified and corrected and the instrument recalibrated.

A quality control sample (QCS) obtained from an outside source must first be used for the initial verification of the calibration standards. Before any laboratory can use this method it must demonstrate that the mean concentrations from three analyses of the QCS are within 5 % of the stated values. The required frequency for the analysis of QCS is quarterly but it is this laboratory practice to analyze QSC with every batch run.

Laboratory fortified blank (LFB): The laboratory must analyze at least one LFB with each batch of samples. If 1 ml of ICM 240 is use the analytes concentrations would be as follow K=1.0, Ag=0.05 and the rest of elements= 0.2 ppm, the LFB recovery must be between 85-115% or within the statistical control limit of mean% recover ± 3 STDEV (Standard deviation), whichever is lower. The number of the data points use to determine the STDEV are between 20 to 30 and the STDEV is updated whenever a new set of 5-10 new data points are available.

Any analyte falls outside the required control limits; source of the problem should be identified and resolved before continuing analyses.

Laboratory fortified matrix (LFM) Run matrix spike sample at a frequency of one and a duplicate per matrix batch of 10 samples. The spike concentrations should be the same as those of the LFB. The spike recovery should be within 70% to 130% of the true value. Do not calculate the percent recovery for constituent that the spike amount is lower than 30 % of it background value. The maximum relative percent different (RPD) allowed for LFM and its duplicate is 15%.

The upper limit of the linear dynamic range has to be established before this method can be used. This could be achieved by running the standard with increasing concentration against a normally run calibration set (one blank and three mixed calibration standards). The upper limits LDR are the highest concentrations for each element where recovery is equal or greater than 90% of the expected values. The upper LDR for the Varian Vista-pro ICP are list in table 1. Any samples that has its concentration exceeds 90% of the upper LDR has to be diluted and reanalyzed.

12. Lowest Reporting Level

ML and MDL for metals by EMD lab at HTP are listed in page 11 of this SOP.

13. Precision and Accuracy

The Quality Assurance Branch (QAB) of the Environmental Monitoring Systems Laboratory – Cincinnati (EMSL-CI), conducted an interlaboratory study of metal analyses by this method. Synthetic concentrates containing various levels of the twenty-five elements listed in Table 4 were added to reagent water, surface water, drinking water and three effluents. These samples were digested by either the total digestion procedure or the total recoverable procedure.

14. References

EPA Method 200.7, 1994

EPA Method 6010B, 1996

SM 3120B, Metals By Plasma Emission Spectroscopy, Standard Method for the Examination of Water and Wastewater, 18 th

15. Appendices

TABLE 1: WAVELENGTHS, INSTRUMENT DETECTION LIMITS

Analyte	Detection WavelengthLimit (nm)	(DI water) mg/l	Reporting & ML Limit mg/l	Upper LDR Limit mg/L
Aluminum	308.215	0.008	0.20	200
Antimony	206.833	0.002	0.05	20
Arsenic	193.759	0.008	0.01	20
Barium	493.409	0.0005	0.01	10
Beryllium	313.042	0.0005	0.002	10
Cadmium	226.502	0.0005	0.01	10
Calcium	315.887	0.018	0.20	50
Chromium	205.552	0.001	0.010	10
Cobalt	228.616	0.0005	0.01	10
Copper	324.754	0.001	0.01	10
Iron	259.940	0.014	0.10	10
Lead	220.353	0.002	0.005	10
Magnesium	279.078	0.008	0.20	40
Manganese	257.610	0.001	0.01	10
Molybdenum	202.032	0.001	0.01	10
Nickel	231.604	0.0005	0.02	10
Potassium	766.491	0.031	0.20	100
Selenium	196.026	0.004	0.01	20
Silver	328.068	0.0005	0.01	2.5
Sodium	589.592	0.051	1.0	120
Strontium	407.771	0.0005	0.01	10
Thallium	190.794	0.0005	0.01	10
Vanadium	292.401	0.0005	0.01	20
Zinc	213.857	0.006	0.02	10
Tin	189.927	0.006	0.01	10

a. The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

References

EPA Method 6010B, 1998
EPA Method 200.7 Revision 4.4

ENVIRONMENTAL MONITORING DIVISION
Hyperion Treatment Plant - Instrumental Chemistry Section – Metals
Laboratory

**STANDARD OPERATING PROCEDURE for INDUCTIVELY
COUPLED PLASMA-MASS SPECTROSCOPY METHOD
FOR TRACE ELEMENT ANALYSIS OF WATER AND
WASTES**

(EPA Methods 200.8, Rev. 5.4)

EMD SOP# 6200.8

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Signature:

Quality Assurance Manager: Jeff Beller
Signature:

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1.0 SCOPE AND APPLICATION

This Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) method may be used for the determination of dissolved and total recoverable elements in ground water, surface water, domestic and industrial wastewaters. This SOP is based primarily on 1994 Revision 5.4 of EPA Method 200.8. User of this SOP should be familiar with EPA method 200.8 (Rev. 5.4 and Rev. 5.5), EPA method 200.2, EMD SOP # METALS 6200.8, EMD SOP # METALS 0024 and also with the Region 9 EPA SOP 507, SOP 403 and SOP 405.

To confirm approval of this method for use in compliance monitoring programs [e.g., Clean Water Act (NPDES)] consult the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES), the latest Federal Register announcements, and the Region 9 EPA Interim Approval of Method 200.8 in October 2002.

Dissolved elements are determined after filtering with a 0.45um pore-size membrane filter and then acidifying the filtrate to match the acid matrix of the calibration standards.

With the exception of silver, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU (nephelometric turbidity units) at the time of analysis. This total recoverable determination, procedure is referred to as "direct analysis".

For the determination of total recoverable elements in aqueous samples as well as in sludge and soil samples, digestion is required (EMD SOP # METALS 0024). The digestion techniques described in this SOP will dissolve almost all elements that could become "environmentally available" but would not dissolve elements, bound in silicate structures, considered as "not mobile" in the environment. Since digestion increases the dissolved solids content of the samples, appropriate steps must be taken to reduce potential interference and prevent damage to the electron multiplier detector by diluting the sample or reducing sample volume to ensure that dissolved solids do not exceed 0.2% (w/v).

Aqueous samples containing suspended or particulate material $\geq 1\%$ (w/v) should be digested as solid sample.

The total recoverable sample digestion procedure is suitable for determination of silver concentration up to 0.1 mg/L. If aqueous samples contain higher silver concentration, smaller well mixed aliquot should be used to bring the silver concentration in analysis solution to less than 0.1 mg/L. Solid samples containing concentrations of silver > 50 mg/kg should be treated in a similar manner.

The total recoverable sample digestion procedure will solubilize and hold in solution only minimal concentration of barium in presence of free sulfate, so barium analysis should be completed as soon as possible after sample digestion.

The total recoverable sample digestion procedure is not suitable for the determination of volatile organo-mercury compounds.

This method, approved for use in compliance monitoring programs [e.g. the Federal National Pollution Discharge Elimination System (NPDES)], is required by SWRCB that the lowest standard concentration in the calibration curve be equivalent to the adopted Minimal Levels (MLs) specified in table 1.

Table 1 lists elements for which this method applies with instrument detection limits (IDL), method detection limit (MDL), minimum level (ML) and upper linear dynamic range (ULDR) using Perkin Elmer Elan 9000 ICP-MS.

2.0 SUMMARY OF METHOD

An aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved materials, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. For total recoverable analysis of biosolids, analytes are solubilized by refluxing with nitric acid. Organic materials in the sample are then oxidized with hydrogen peroxide, and analytes are further solubilized by refluxing with hydrochloric acid. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in sample where turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

The method describes a technique of multi-element determination of trace elements by ICP-MS. Liquid samples are nebulized and the produced aerosol is transported to the plasma torch where desolvation, atomization and ionization occur. The resulting ions (primarily singly charged positive ions) are then extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer. The ions transmitted through the quadrupole are then detected with a dynode electron multiplier detector and the ion information processed by a data handling system, which takes into account of polyatomic ions interferences and isobaric elemental interferences. Internal standards are used to compensate for instrumental drift and erroneous signal enhancement or suppression caused by sample matrix.

3.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements by ICP-MS. They include mass spectral interferences and physical interferences. Mass spectral interferences can be categorized as isobaric elemental interferences, isobaric polyatomic ion interferences, and abundance sensitivity.

Isobaric Elemental Interferences occur when isotopes of different elements form singly or doubly charged ions which have the same nominal mass-to-charge ratio and which cannot be resolved (i.e. separated) by the mass spectrometer. However, most elements determined by this method have at least one isotope that is free of isobaric elemental interference. Of the analytical isotopes used in the method only molybdenum-98 (ruthenium-98) and selenium-82 (krypton-82), antimony-123 (technetium-123) have isobaric elemental interference. For isotopes that must be monitored, only cadmium-114 and indium-115 have isobaric interference from tin. Correction of data for these isotopes are made by measuring the signal from another isotope of the interfering element and using its natural abundance ratio to calculate the intensity to be subtracted from the signal of the isotope of interest. Usage of high purity krypton-free argon will greatly reduce the effect of krypton-82 on selenium-82 analysis.

Isobaric Polyatomic Ion Interferences: These are caused by molecular ions that have the same nominal mass-to-charge ratio as the isotope of interest and which cannot be resolved by the mass spectrometer. Most of these ions have been identified; they are commonly formed in the plasma or interface system from support gases or sample components. These interferences must be recognized, and corrections to the data must be performed. The equations for these corrections need to be established at the time of analysis, since they are dependent on sample matrix and instrument operating conditions. The presence of chloride in sample results in the formation of singly charged ions $^{40}\text{Ar}^{35}\text{Cl}$, $^{35}\text{Cl}^{16}\text{O}$, $^{37}\text{Cl}^{16}\text{O}$ that interfere respectively with ^{75}As , ^{51}V , and ^{53}Cr . Although correction for interference of $^{40}\text{Ar}^{35}\text{Cl}$ on the analytical isotope ^{75}As can be made using the signal for $^{40}\text{Ar}^{37}\text{Cl}$ and the correction for $^{35}\text{Cl}^{16}\text{O}$ on the isotope ^{51}V can be performed using the signal for $^{37}\text{Cl}^{16}\text{O}$, no correction can be made for the interference of $^{37}\text{Cl}^{16}\text{O}$ on the monitored isotope ^{53}Cr . Interference of $^{95}\text{Mo}^{16}\text{O}$ on the monitored isotope ^{111}Cd can be corrected using the signal for $^{92}\text{Mo}^{16}\text{O}$. The presence of bromide in sample can result in the formation of $^{81}\text{Br}^1\text{H}$ that will elevate recovery for Se at mass 82. If this correction is required then bromine at mass 79 and 81 need to be added to this method and monitored.

Abundance Sensitivity is defined as the degree to which the wings of a large ion peak contribute to an adjacent ion peak. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. The spectrometer resolution should be adjusted to minimize these interferences.

Physical interferences are generally associated with the sample transport into the plasma, sample conversion processes in the plasma, and transmission of ions from the plasma through the interface into the mass spectrometer. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), in the process of aerosol formation and transport into the plasma (e.g., surface tension effects), and during excitation and ionization processes in the plasma. Such differences in viscosity and surface tension between samples and standards can cause significant inaccuracies especially if samples contain high dissolved solids. Internal standardizations are used to compensate for these physical interferences. High levels of dissolved solids in the sample may contribute deposits of material on the sampler cone and the skimmer cone reducing the effective diameter of the orifices and therefore the ion transmission. Samples should be diluted if dissolved solids levels exceed 0.2% (W/V).

Memory interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, and from the buildup of sample material in the plasma torch and spray chamber. The possibility of memory interference should be recognized within an analytical run and suitable rinse times should be used to reduce them. Memory interferences may be assessed within an analytical run by looking at the values of the three replicates. If the integrated signal values drop consecutively, the analyst should examine the analyte concentration in the previous sample to identify the possibility of a memory effect. If previous sample has high concentration, the sample should be reanalyzed after a long rinse period. In the determination of mercury, gold at 100 ppb is to be added to rinse solution to minimize memory effect.

4.0. SAMPLE COLLECTION, PRESERVATION AND PREPARATION

- 4.1. Prior to the collection of an aqueous sample, consideration should be taken to the type of data desired (i.e. dissolved, total or total recoverable) so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or “direct analysis” to ensure that the sample has been properly preserved. If properly acid preserved, the sample can be held up to 6 months.
- 4.2. For the determination of dissolved elements, the sample must be filtered through a 0.45 μm pore-size membrane filter as soon as practically possible after collection. Acidify the filtrate immediately following filtration with (1 + 1) HNO_3 , to a pH of 2 or lower.
- 4.3. For the determination of total recoverable elements, the samples are not filtered but acidified with (1+1) HNO_3 , to pH 2 or less as soon as possible. Following acidification, the sample should be mixed, held for sixteen hours, and then verified to be pH < 2 just prior to withdrawing an aliquot

for analysis. If for some reason the pH is verified to be higher than 2, more acid must be added and the sample held for sixteen hours until verified to be pH < 2.

- 4.4. Aqueous samples containing suspended or particulate material > 1% (w/v) should be extracted as a solid type sample.
- 4.5. Sample preparations for dissolved elements are suitable filtration through a 0.45 µm pore diameter membrane filter, acid preservation and then dilution to a predetermined volume. Analytes may be analyzed directly without acid digestion of samples. Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form soluble chloride complex. Therefore hydrochloric acid should be added to filtered samples to keep silver in solution (1 mL of HCl to 50 mL of sample) and analysis should be completed as soon as possible after sample preparation. If low recoveries of silver occur in fortified sample matrices, it is recommended that samples be digested prior to the determination of silver. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v).

Sample preparation for total recoverable analytes must include a digestion/extraction step (EMD SOP # METALS 0024).

5.0 APPARATUS

- 5.1. Inductively Coupled Plasma-Mass Spectrometer (Perkin Elmer SCIEX ELAN 9000).
- 5.2. Dell Optiplex Personal Computer Hardware/ Perkin Elmer ELAN Data Station-Instrument Control Software Version 2.4 1994-2001
- 5.3. Perkin Elmer AS-93plus Auto-sampler
- 5.4. PolyScience Recirculator/Chiller Model Number 3370
- 5.5. Either liquid or gaseous argon, purity 99.996%, oxygen < 5 ppm, hydrogen <1 ppm, nitrogen <20 ppm, water < 4 ppm.

6.0 REAGENTS AND STANDARDS

- 6.1 Concentrated acids used in the preparation of standards and for sample processing must be ultra-high purity grade or equivalent (Fisher Scientific – Optima grade, J.T. Baker - Ultrex grade.)
Hydrochloric acid-concentrated (sp. gr. 1.19)
Nitric acid-concentrated (sp. gr. 1.41).

- 6.2 Deionized water, used in the preparation of all reagents and obtainable from the central water purification system of the Pregerson Laboratory Building, is prepared by passing potable water through a mixed bed of cation and anion exchange resins, and has purity equivalent to ASTM Type I grade water.
- 6.2 1:1 (vol/vol) nitric acid prepared by adding 25 ml concentrated nitric acid to 25 ml reagent water in a clean 50 ml vial.
- 6.3 Tuning solution 10 ppb of Mg, Rh, In, Ba, Ce, Pb, U.
The tuning solution may be purchased from Perkin Elmer or prepared from 1000 ppm single element stock solutions.
- 6.4 Internal Standard Stock Solutions
Solution 1: 10 ppm Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y in 1% nitric acid.
Solution 2: 50 ppm Ge, 10 ppm Rh. in 1% nitric acid.
The Internal Standard Stock solutions may be purchased or prepared from 1000 ppm single element stock solutions.
- 6.5 Internal Standard Working Solution. (400 ppb Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y; 1000 ppb Rh; 5000ppb Ge in 1% nitric acid).
Prepare by pipetting :
1.00 ml HNO₃ 1/1,
2.00 ml Internal Standard Stock Solution 1,
5.00 ml Internal Standard Stock Solution 2,
and dilute to 50 ml with reagent water.
- 6.6 Auto-lens solution. 10 ppb Be, Co, In, U.
The Auto-lens solution may be purchased or prepared from 1000 ppm single element stock solutions.
- 6.7 Standard Stock Solutions
ML Stock Solution 1: 20 ppm As, Se; 10 ppm Tl, Ni, Zn; 5 ppm Sb, Be, Cr, Cu, Pb; 2.5 ppm Cd, Ag.
Prepare from 1000 ppm single element stock solutions.
- 1 ppm Stock Solution (IPC 1+2 1ppm): 1 ppm As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 0.125 ppm Ag. Prepare by pipetting 2.0 ml HNO₃ 1/1, 0.50 mL IPC-1(Inorganic Ventures, Inc), 0.50 mL IPC-2 (Inorganic Ventures, Inc) and diluting to 100 mL with reagent water.

Calibration Standards.

Prepare fresh calibration standards daily. Four standards and one calibration blank are used for the calibration of the instrument.

Calibration Blank.

Fill a 50 mL vial with approximately 20 mL of reagent water. Pipette 1 mL of 1/1 HNO₃, 1.0 mL of Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 1 (ML):

2 ppb As, Se; 1 ppb Tl, Ni, Zn; 0.5 ppb Sb, Be, Cr, Cu, Pb; 0.25 ppb Cd, Ag.

Prepare a ML Stock Solution 2 by pipetting 2 mL HNO₃ 1/1, 1.0 mL of the ML Stock Solution 1 (20 ppm As, Se; 10 ppm Tl, Ni, Zn; 5 ppm Sb, Be, Cr, Cu, Pb; 2.5 ppm Cd, Ag) and diluting to 100 mL with reagent water.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO₃, 0.50 mL of the ML Stock Solution 2, 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 2:

10 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 1.25 ppb Ag.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO₃, 0.50 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 3:

20 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 2.50 ppb Ag.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO₃, 1.0 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

Calibration Standard 4:

100 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 12.5 ppb Ag.

Fill a 50 mL vial with approximately 20 mL of reagent water, add 1 mL HNO₃, 5.0 mL of the 1 ppm Stock Solution (IPC 1+2), 1.0 mL of the Internal Working Solution and dilute to 50 mL with reagent water.

The acceptable correlation coefficient of linearity for each calibration is 0.998 or greater.

6.8. Quality Control Sample (To verify calibration standards).

Quality Control Stock Solution (ICM 240):

1 ppm As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 0.250 ppm Ag.

Prepare by pipetting 2 mL HNO₃ 1/1, 5.0 mL of ICM-240 (Ultra Scientific) and diluting to 100 mL with reagent water.

Quality Control Working Solution (ICM 240):

20 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Sr, Tl, V, Zn, Sb, Mo, Sn; 5.00 ppb Ag.

Prepare by pipetting 1 mL HNO₃ 1/1, 1.0 mL of the Quality Control Stock Solution, 1.0 mL of the Internal Working Solution and diluting to 50 mL with reagent water.

6.9 Analog Stage Detector Optimization Solution.

Prepare 100 ppb Mg solution in 1% HNO₃ by pipetting 1 mL HNO₃ 1/1 and 0.005 mL of 1000 ppm Mg into a 50 mL vial and dilute to 50 mL with DI water.

6.10 Dual Detector Cross Calibration Solution:

200 ppb As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Sr, Tl, V, Zn, Sb, Mo, Sn; 25 ppb Ag.; 8 ppb Bi, Ho, In, Li6 (95 % enriched) Sc, Tb, Y; 20 ppb Rh; 100 ppb Ge; 4 ppm Se in 1% nitric acid.

Prepare by filling a 50 mL vial with approximately 20 mL of DI water, and adding 1 mL HNO₃ 1/1, 5 mL of the IPC 1+2 Stock Solution (2ppm), 0.20 mL of 1000 ppm Se, 1 mL of the Internal Standard Working Solution and dilute to 50 mL with DI water.

7.0 SAFETY

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Wear glove when handle samples and chemicals.

Never view the ICP torch directly without protective eyewear. Potentially hazardous ultraviolet radiation may be emitted. Safety glasses will in general provide sufficient protection.

ICP-MS instrument generates high amounts of radio frequency energy in the RF power supply and torch box, which is potentially hazardous if allowed to escape. Safety devices and screening interlocks should not be bypassed or disconnected.

The power supply for the operation of ICP-MS is capable of generating potentially lethal voltages. No maintenance should be performed when the power is on.

Ensure that the exhaust system is working properly. The Elan 9000 ICP-MS requires two vents, one for the ICP power supply/roughing pump exhaust and another vent for the torch box exhaust. Exhaust venting is important not only to remove heat produced by the ICP torch, RF power supply and pump motors, but also to protect laboratory personnel from toxic vapors that may be produced by ICP.

Gas cylinders must be clearly marked to identify the status (e.g. full, empty, etc...), carefully secured and stored away from heat. Since cylinders have pressure-relief device that might release argon, room ventilation should be adequate to prevent accumulation of non-life-sustaining gas.

8.0 PROCEDURE

8.1 Check the following before startup:

Water chiller

Exhaust system

Vacuum roughing pumps

Cold vacuum(should be in 10^{-6} torr range). Record pressure reading in log-book.

Argon tank

Sample introduction system (pump tubing, nebulizer, spray chamber, torch, cone, etc...)

- 8.2 Initiate the plasma and allow a warm-up for at least 30 minutes. The tuning procedures may be carried out during warm up. Check out the following during warm-up:
Operating vacuum. Record value in log-book.
Nebulizer gas flow rate
Sample uptake rate
Spray chamber drainage
- 8.3 Open the EMD-Daily performance workspace and open the EMD-Daily method
Aspirate the 10 ppb tuning solution.
Click on the Analyze button in manual sample window.
Check that the RSDs for five replicates for all Be, Mg, Co, In, Rh and Pb are less than 5%.
Check that the background at mass 220 is < 30 cps.
Check that % oxides < 3%.
Check that % double charge < 3%.
Mg Intensity > 100,000 cps (140,000 cps, normally)
Rh Intensity > 400,000 cps (600,000 cps).
In Intensity > 400,000 cps (700,000 cps)
Pb Intensity > 300,000 cps (450,000 cps).
If the instrument performance check passes, go to 8.11 and proceed with the samples.
- 8.4 If the instrument performance check does not pass, open the EMD- X-Y workspace and the EMD-X-Y method, open the real-time window by clicking on realtime icon, aspire the tuning solution and make X-Y adjustment for maximum Rh intensity. This procedure is only necessary when cones or torch have been changed.
- 8.5 Open the Neb-power-Lens-Oxide workspace and the EMD-Optimize method, set the RF power to 1000-1100 watts for clean water, 1200-1400 watts for soil and sediments digests and optimize the following parameters using the tuning solution:
Optimize the nebulizer argon flow.
Optimize the static lens voltage (optional).
Save the optimization file.
- 8.6 Open the EMD-Auto-Lens-Calibration workspace and the EMD-Autolens Calib method and perform auto-lens calibration using the Auto-lens Solution as the following:
Clear the old calibration.
Click on Get Analytes.
Click on Calibrate.

Save the optimization file, print the current settings in the default.dac using <File><Print> option and the Optimization.rop.
Go to 3 and perform Daily Performance Check.

- 8.7 Perform a Pulse Stage Detector Optimization.
Open the EMD Pulse Stage Optimization workspace and the EMD Optimize method.
Optimize Pulse Mode Voltage using Tuning Solution as follows:
Aspire the tuning solution.
Click on Pulse Stage Voltage tab.
Click on Get Analyte List, check that Rh appears in the Analyte field.
Select the start and end values of the potential set points at 900 and 1000 respectively and set the step value at 25.
Select Intensity Change Percent at 15% as optimization criteria.
Click on Optimize tab.
Save the Optimization file.
In the interactive window, a plot of pulse intensity vs. pulse stage voltage is displayed. The optimum point is indicated by a diamond symbol. Check that the software selected the correct point. Do not operate the detector at voltages far beyond the saturation point as this can reduce detector lifetime, cause signal drift and increase noise level.
This procedure is only required when a new detector is installed or detector voltages need to be optimized for higher sensitivity.
- 8.8 Analog Stage Detector Optimization.
Analog Stage Detector must be performed before performing Dual Detector Calibration. Pulse stage optimization must be performed before and after an analog stage optimization.
Open the EMD Analog Stage Optimize workspace and the EMD Analog Stage Optimization method.
Chose Analog Stage Voltage in the parameter Description box.
Click on Get Analyte List, make sure that Mg appears in the Analyte List.
Select Auto and Full in the Optimization Criteria group. Type in 12500 for the Target Gain or select Use Nmax and type in 1e9 for the target Nmax.
Aspire 100 ppb Mg solution then click on Optimize.
If the optimization is successful, a message appears stating that the optimization is complete. Save the optimization file.
- 8.9 Dual detector crossed calibration. Dual detector calibration is used to extend the dynamic range of the detector by normalizing the analog stage of the detector to the pulse stage. This procedure is required whenever the analyte concentrations that are needed exceed the linear dynamic range of the pulse counting.
Optimize Pulse Stage detector voltage, Analog Mode Voltage and again Pulse Stage detector voltage.

Open the EMD Dual Detector Calibration workspace. Select the EMD Dual Detector Calibration method. Check to make sure that the method contains all elements you want and there are no interference equations in the method.

If analytes are already listed on the Dual Detector Calibration page, click on Clear Calibration and then on Get Analyte List.

Enter the Start Value (-1 to -3), the End Value (8 to 12) and the step value (0.25 to 0.5) in the Lens Voltage group.

Aspire the Dual Detector Cross Calibration Solution.

Click on Calibrate tab.

The ELAN will perform 2 separate acquisitions:

The first acquisition is used as the calibration blank (lens voltage is set for zero ion transmission) and the dataset name is label Dual Calibration Blank.

The second acquisition is the actual dual calibration.

One can view the analysis progress in the real time window in Signal or Numeric Mode.

In the Interactive window, one can view the cross calibration curves for 1 to 5 isotopes plus the Pulse/Analog Gain Interpolation curve. The correlation coefficients for individual isotopes are normally at least 0.9995. Save the optimization file.

8.10 Tuning (Mass Calibration. & Resolution)

Tuning of the Elan 9000 should be performed monthly and whenever there are changes to the ELAN's electronics or if there are needs to modify resolution for one or more elements.

Open the EMD Tuning workspace.

Open the EMD-tuning method.

Aspire the tuning solution.

Click on Tuning icon to display the Tuning window, make sure the tuning file has all the required elements in the method (He, Mg, Rh, Pb, U, Ce) and that the Measure Peak Width Only parameter is toggled Off.

Click on the Tune Mass Spec button in the tuning window to perform a full Autotune, adjusting both the mass calibration and the resolution.

Click on the Interactive icon to display the spectra of all tuning analytes.

Save the Tuning file.

Print the results of mass calibration and resolution adjustment using the Tuning.rop report format.

Check that the measured mass values remain within 0.05% of the actual mass and peak widths are approximately 0.70 amu.

In selected instances, it may be desirable to use resolution settings that are different from the default 0.7 amu. Click in the Resolution DAC value cell for the analyte you want to adjust, increase the DAC value to increase resolution (narrower the peak) or set the DAC to a smaller value to decrease the peak resolution (broaden the peak). Aspire the tuning solution and click on Tune Mass Spec to perform a full Auto-Tune.

8.11 Quantitative Analysis.

Open the EMD Quantitative Analysis workspace.

Click on method icon and open the 200.8EMD method.

Enter report file name in the Report page of the method.

Click on the green R icon to view files currently in use and chose Load Dataset to select an existing dataset for the month (Feb03 for the month of February 2003 for example) or New Dataset to create a new dataset.

Prepare blank, calibration standards and load them into the auto-sampler positions 1-5 (position 1 for calibration blank; position 2 for standard 1, ML; position 3 for standard 2, 10 ppb; position 4 for standard 3, 20 ppb; position 5 for standard 5,100 ppb).

Prepare the quality control sample ICM-240, 20 ppb and load it into position 6.

Edit the Sample window and enter sample information in the batch sample page (sample name, LIMS ID, dilution factor). The frequency of QC solution analyses (e.g. calibration blank, instrument performance check solution, quality control sample, etc...) is already set in the method, so there is no need to enter QC information in sample window.

The measurement action for the first sample must be “analyze blank, standards, and samples”. Measurement action for all other samples is “analyze sample”. Enter appropriate pump speeds for all samples. Save sample file and reopen the sample file (this must be done for the batch QC to run properly).

Prepare sample by filling a 50 mL vial with approximately 10 mL of reagent water, add 1 mL HNO₃, 1.0 mL of the Internal Working Solution, add an exact volume of digested sample (2.5 mL for 1:20 dilution or 5 mL for 1:10 dilution) and dilute to 50 mL with reagent water. Final volume is not critical since internal standards are used, so accuracy of the markings on the side of each vial is sufficient.

Load the samples into the auto-sampler positions specified in the sample file. Select the samples to be analyzed by highlighting the row number with the mouse and start the analysis by clicking on “Analyze Batch”.

9.0. CALCULATION

Elemental equations for corrections of masses interference are:

Element	Mass in amu	Corrections
Vanadium	50.944	$-3.127(^{37}\text{Cl}^{16}\text{O} - (0.113 \times ^{52}\text{Cr}))$
Arsenic	74.922	$-3.127(^{40}\text{Ar}^{37}\text{Cl} - (0.873 \times ^{82}\text{Se}))$
Selenium	81.917	$-1.008696 \times ^{83}\text{Kr}$
Molybdenum	97.906	$-0.110588 \times ^{101}\text{Ru}$
Cadmium	110.904	$-1.073(^{92}\text{Mo}^{16}\text{O} - (0.712 \times ^{106}\text{Pd}))$
Cadmium	113.904	$-0.026826 \times ^{118}\text{Sn}$
Indium	114.904	$-0.014032 \times ^{118}\text{Sn}$
Antimony	122.904	$-0.127189 \times ^{125}\text{Te}$
Lead	207.977	$+ ^{206}\text{Pb} + ^{207}\text{Pb}$

Data should be calculated by application of internal standardization.

Reagent blank should be subtracted from all samples. This is particularly important for digested samples requiring large quantities of acids to complete the digestion.

If dilutions were performed, the appropriate factor must be applied to sample values.

Sample data should be reported in unit of $\mu\text{g/l}$ for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL. For data values less than ten, two significant figures should be use for reporting element concentrations. For data values equal or greater than ten, three significant figures should be used.

The isotopes recommended for analytical determination are:

^9Be , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{60}Ni , ^{63}Cu , ^{66}Zn , ^{75}As , ^{82}Se , ^{117}Sn , ^{98}Mo , ^{107}Ag , ^{111}Cd , ^{123}Sb , ^{137}Ba , ^{205}Tl , ^{206}Pb , ^{207}Pb , ^{208}Pb .

If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interference than the primary

recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

The QC data obtained during the analysis provide an indication of the quality of the sample data and should be provided with the sample results.

10.0. DATA MANAGEMENT

The metals lab uses method 200.8 for the determination of Ag, Pb, Sb and Tl in the monthly and weekly treatment plants effluent samples. Raw data are stored by ICP-MS software under the filename "c:\elandata\reportoutput\yyyymmdd". For data reduction, the same data are transferred to "EMDB\ICP-MS\2004" using the Excel Template, developed for the metals lab, and the processed data stored in "EMDB\ICPMS_DATA\2004. Manipulation for the final concentrations and for displayed QC data could be performed thru the master sheet on the excel file. The printout data are kept in a three ring binder folder as permanent record. Final results are reported in Laboratory Information Management System.

11.0. QUALITY CONTROL

11.1 Initial Demonstration of Laboratory Performance. The initial demonstration of performance is used to characterize instrument performance and laboratory performance prior to analyses conducted by this method.

11.1.1 Linear Calibration Range.

Linear Calibration Range should be determined before using the ICP-MS for producing any legal reporting data, and whenever there are changes in the detector voltages, RF generator, sample introduction system (change in nebulizer or spray chamber type).

Calibrate the instrument as usual, and run a series of increasing concentration standards. The upper linear dynamic range (ULDR) limit is defined as the concentration where the measured value is within 10% of the actual prepared value of the standards. Care should be taken to avoid potential damage to the detector during this process. ULDR are listed in table 1. When analyze sample that has concentrations of any element greater than 90 % of the ULDR that sample must be diluted and reanalyzed.

11.1.2 Quality Control Sample.

On a quarterly basis, to verify the calibration standards and acceptable instrument performance, it is required to analyze a Quality Control Sample (QCS). The determined mean concentration from 3 analyses of the QCS

must be within 10% of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the second analysis is unacceptable, problem must be identified and corrected.

11.1.3 Instrument Detection Limits (IDLs)

IDL should be determined whenever there is any significant change to the instrument. Calibrate the instrument. Run a blank as if it were a sample for a series of 10 sequential measurements with rinsing in between each measurement. Calculate the standard deviation and multiply by 3 to obtain the IDL. IDL are listed in table 1.

11.1.4 Method Detection Limits (MDL)

MDL should be established for all analytes using reagent water fortified at a concentration of two to five times the estimated detection limit. Analyze seven replicate aliquots of the fortified reagent water that have been processed through the entire analytical method and calculate the MDL as follows:

$$\text{MDL} = t \times (\text{Standard Deviation of the replicate})$$

Where t is the Student's value for a 99% confidence level with n-1 degrees of freedom (t = 3.14 for seven replicate). MDL are listed in table 1. The determination of MDL in reagent water represents a best-case situation and does not reflect possible matrix effects of real samples. The MDLs must be sufficiently low to be able to detect analytes at the required levels according to compliance monitoring regulation. MDLs should be determined annually or whenever there is a change in instrument operating conditions.

11.2. Mandatory Laboratory Performance Quality Assurance Procedures

11.2.1. Laboratory Reagent Blank (LRB)

Laboratory Reagent Blank (LRB) is an aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if analytes or other interferences are present in the laboratory environment, reagents, or apparatus. A minimum of one LRB must be run with each batch of 20 samples of the same matrix. LRB values greater than the MDL indicate laboratory or reagent contamination. The values of LRB and their standard deviations must be kept on file and be available for review.

The upper control limit for LRB can be developed when a minimum of 20 data become available as follows:

$$\text{Upper Control Limit} = \bar{x} + 1.5 S$$

Where \bar{x} is the mean of LRB and S is the standard deviation of the mean LRB.

For NPDES test program, whenever LRB values constitute 10% or more of the analyte level determined for the sample or is 2.2 times the analyte MDL, whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

11.2.1. Laboratory Fortified Blank (LFB)

Laboratory Fortified Blank is an aliquot of reagent water to which known quantities of the analytes are added. The LFB is treated and analyzed exactly like a sample. The purpose of analyzing LFB is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery using the following equation

$$\text{Rec.} = (\text{LFB} - \text{LRB}) / S \times 100$$

Where: Rec. = Percent Recovery

LFB = Lab. Fortified Blank Result

LRB = Lab. Reagent Blank Result

S = Concentration of analyte added to fortify the LRB

The percent recovery for the LFB should be within the required control limits of 85% - 115%. If the recovery is not in control, the source of the problem should be identified and resolved before analysis is continued. The percent recoveries of LFB and their standard deviations must be kept on file and be available for review.

Optional upper and lower control limits can be developed when a minimum of 20 performance data become available as follows:

$$\text{Upper Control Limit} = \bar{x} + 3 S$$

$$\text{Lower Control Limit} = \bar{x} - 3 S$$

Where \bar{x} is the mean percent recovery of LFB and S is the standard deviation of the mean percent recovery.

The optional control limits must be equal to or better than the required control limits of 85% - 115%. After each five new recovery measurements, new control limits are calculated using the most recent 20 data points. For simplification and due to the rather low number of batches run by this lab, annual updating of ongoing control limits is accepted.

11.2.2. Instrument performance check (IPC)

For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration, run the calibration blank and calibration standards (10 ppb or 20 ppb) as surrogate samples immediately following each calibration routine, after every ten samples and at the end of the sample run. The analysis of all analytes within the standard solutions must be within 10% of the calibration. If the calibration cannot be verified within the specified limits, the instrument must be re-calibrated. If the continuing calibration check is not confirmed within 15%, the previous ten samples must be re-analyzed after recalibration. If the sample matrix is responsible for the calibration drift, the previous 10 samples should be reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

11.3. Assessing Analyte Recovery and Data Quality

11.3.1 Laboratory Fortified Sample Matrix (LFM).

Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of data. LFM procedure is required to assess these effects. Known amounts of analytes are added to a minimum of 10% of the samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and analytes added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank or 1-5 times the background concentration, whichever is greater. Percent recovery for each analyte, corrected for background concentration, is calculated using the following formula:

$$R = (C_s - C) \times 100 / S$$

Where R = percent recovery

C = sample background concentration

C_s = fortified sample concentration

S = concentration of analyte added to fortify the sample

The LFM range is 70% - 130%. Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration.

Optional upper and lower control limits can be developed when a minimum of 20 performance data become available as follows:

$$\text{Upper Control Limit} = x + 3 S$$

$$\text{Lower Control Limit} = x - 3 S$$

Where x is the mean percent recovery of LFM and S is the standard deviation of the mean percent recovery. The optional control limits must be equal to or better than the required control limits of 70% - 130%. After each five new recovery measurements, new control limits are calculated using the most recent 20 data points.

If the recovery falls outside the designated range and laboratory performance is shown to be in control (Sect. 11.2), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for the unfortified sample is suspect, due to either the heterogeneous nature of the sample or an uncorrected matrix effect.

11.3.2. Internal Standard Responses.

The analyst is expected to monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increased in the concentrations of individual standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60% - 125% of the original response in the calibration blank. If greater deviations are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze. If after flushing the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible cause of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

12.0 REPORTING LEVEL

A reporting level is the lowest concentration of a detected substance that must be reported for specific regulatory purposes, such as determining compliance with effluent limitations and water quality criteria or objective.

The reporting limit (RL) is obtained by first determining the MDLs. A multiple of MDL level is spiked into reagent water and processed as a sample. If the spike is recovered within 60% and 140%, the test concentration is the lowest RL. The RL for most elements is about five times the MDL and represents a practical and routinely achievable detection limit with a relatively good certainty that any reported value is reliable. If a sample is diluted prior to analysis, the RL is multiplied by the dilution factor.

For NPDES permit testing, the metals lab uses "Minimum Level (ML)" as RL. ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed according to the method. The ML and MDL for this method are listed in [EMD_INFO.METALS. 2003-MDL] 62008.XLS file.

13.0. PRECISION AND ACCURACY

13.1. Precision.

Check that the relative standard deviations of three replicates (Replicate RSD) are less than 5% for standards and samples.

13.2. Accuracy.

To verify the calibration standards, it is recommended to run QCS (ICM-240) at the beginning and at the end of the run. The analysis of a QCS prepared to a concentration of 20 ppb (5 ppb for Ag) must be within 90%-110% of the stated value initially and within 15% at the end. All requirements for laboratory reagent blank (LRB), laboratory fortified blank (LFB), laboratory fortified matrix (LFM) must be satisfied before using the data for reporting.

14.0. REFERENCES

14.1. EPA Method 200.8 Revision 5.4, May 1994, "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry".

14.2. EPA Method 200.8 Revision 5.5 "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry".

14.3. EPA Method 200.8 Using the ELAN 6000/6100 ICP-MS PerkinElmer Spectrometry

14.4. ELAN ICP-MS Hardware Manual, 1995, PerkinELmer.

14.5 Region 9 EPA SOP 507, November 2002

14.6 Region 9 EPA SOP 403, November 2002

14.7 Region 9 EPA SOP 405, November 2002

15.0 APPENDIX

Element	Isotope	ML in ppb	IDL in ppb	MDL in ppb	ULDR in ppb
Be	⁹ Be	0.5	0.01	0.02	30
V	⁵¹ V	1.0	0.02	0.02	200
Cr	⁵² Cr	0.5	0.04	0.06	200
Cr	⁵³ Cr	0.5	0.03	0.05	200
Mn	⁵⁵ Mn	1.0	0.009	0.08	200
Co	⁵⁹ Co	1.0	0.01	0.005	200
Ni	⁶⁰ Ni	1.0	0.01	0.07	200
Cu	⁶³ Cu	0.5	0.009	0.1	200
Cu	⁶⁵ Cu	0.5	0.009	0.1	200
Zn	⁶⁶ Zn	1.0	0.02	0.1	200
Zn	⁶⁷ Zn	1.0	0.04	0.2	200
Zn	⁶⁸ Zn	1.0	0.04	0.1	200
As	⁷⁵ As	2.0	0.04	0.4	200
Se	⁷⁷ Se	2.0	0.1	0.1	200
Sn	¹¹⁸ Sn	1.0	0.02	0.01	200
Mo	⁹⁸ Mo	1.0	0.006	0.01	200
Ag	¹⁰⁷ Ag	0.25	0.002	0.02	25
Cd	¹¹¹ Cd	0.25	0.01	0.02	200
Cd	¹¹⁴ Cd	0.25	0.01	0.01	200
Sb	¹²¹ Sb	0.5	0.02	0.01	200
Sb	¹²³ Sb	0.5	0.01	0.01	200
Ba	¹³⁵ Ba	1.0	0.006	0.03	200
Ba	¹³⁷ Ba	1.0	0.01	0.04	200
Tl	²⁰⁵ Tl	1.0	0.01	0.01	200
Pb	²⁰⁸ Pb	0.5	0.009	0.05	200
Li	⁶ Li	Inter. Standard			
Sc	⁴⁵ Sc	Inter. Standard			
Ge	⁷² Ge	Inter. Standard			
Rh	¹⁰³ Rh	Inter. Standard			
Y	⁸⁹ Y	Inter. Standard			
In	¹¹⁵ In	Inter. Standard			
Tb	¹⁵⁹ Tb	Inter. Standard			

APPENDIX H

Quality Assurance/Quality Control

The quality assurance objectives for measurement of data are unique to the particular program for which the data are collected and utilized. They describe the overall uncertainty that the data user is willing to accept in order to make decisions for environmental or other concerns. This uncertainty describes the data quality that is needed, which are usually expressed in terms of precision, bias, representativeness, comparability, and completeness.

The participating laboratories will use approved and recognized test methods, and comply with uncertainty requirements of the method. Quality control samples are measured and uncertainties are assessed and results must be within the range prescribed by the methods. Internal acceptance criteria are established by analyzing laboratory control samples on a daily basis. The participating laboratories will strive to meet the QA/QC goals described in this section and, therefore, be able to attest to the integrity of the sampling and analytical process.

The following QA/QC procedures are examples for sample collection, laboratory analyses, and data management to ensure the production of reliable and defensible data.

Sample Collection

Only trained laboratory staff will be assigned to collect samples using proper sampling procedures, appropriate sampling equipment, required containers, and proper preservation techniques.

General guidelines for sample collection by laboratory staff are as follows:

- Label sample containers with sample date, sample time, sampling point, sample type (grab/composite), preservatives added (if needed), the name of the sampler, and analyses needed.
- Use aseptic technique when collecting samples to prevent contamination.
- Avoid collecting sample in multiple sweeps and no refilling of the sample bottle.
- Once the sample is collected, immerse at least one-third of the sample bottle in ice.
- Once received, log the samples into the laboratory system as soon as possible, assign a unique login number, and properly store.
- Sample preparation steps done prior to analysis, such as sample preservation are described in individual test SOP's.

Sample Handling

Chain-of-Custody

The purpose of the chain-of-custody is to establish detailed written and legal documentation of all transactions in which samples are transferred from the custody of one individual to another. The custody procedure is also used whenever samples are submitted to a contract laboratory. The chain-of-custody begins at the sample collection site and includes couriers or messengers who handle the sample in transit. It follows the sample in the laboratory until its ultimate disposal. It is a form of proof used to establish the authenticity and integrity of the sample, since the results will be used to show compliance with the TMDL requirements, i.e., numeric targets and wasteload allocations.

A Chain-of-Custody (COC) must accompany each sample submitted to a participating laboratory. If a COC has not been filled out prior to delivery of the sample, a form will be provided to the delivery person prior to acceptance of said sample. The COC will be reviewed to make sure that all of the needed information has been supplied. See appendix F for examples of the Chain of Custody Forms.

Sample Holding & Preservation

Samples must meet EPA holding time requirements for each testing parameter.

After the sample is received, the participating laboratory will enter the sample information into the Laboratory Information Management System (LIMS) or comparable database and a unique laboratory registration number will be generated for that sample.

Sample Disposal

After the analyses are completed the sample will be retained as legal evidence or legally disposed. Analyzed samples and standards used in analyses are disposed of in accordance with the laboratories written procedures.

Analytical Procedures

Analyses

There are many different analytical methods applicable to environmental analyses. As a guide, references for the analytical procedures are listed below.

"Standard Methods for the Examination of Water and Wastewater", 18th – 20th edition, 1992 and 1998 respectively, APHA, AWWA, WPCF, Washington, DC.

"Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, revised March 1983.

Test Methods for Evaluating Solid Waste. 1986. Revision December 4, 1996. Volume IB: Laboratory Manual Physical/Chemical Methods, 3rd Edition. United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Washington, D.C.

Standard Operating Procedures (SOPs)

Routine analyses are defined in Standard Operating Procedures (SOPs), which are detailed descriptions of how to use and what to expect from a method. They contain method-specific QC criteria (i.e., instrument calibration, reagent blank, method blank, calibration standards, etc.), and QC requirements such as duplicate analysis, spike recoveries, holding time, etc. See Appendix F for examples of this type of documents.

2.1 System and Performance Audits

An audit is a periodic check to ensure that the laboratory operates according to the policies and procedures described in the Quality Assurance Manual, complies with good laboratory practices, and meets the requirements of regulatory agencies. It may be either a system or performance audit.

System Audit

A system audit is a review of laboratory operations conducted to verify that the laboratory has the necessary facilities, equipment, staff, and procedures in place to generate acceptable data. It is an on-site inspection of the laboratory's system of operations. It may be an internal or external audit. Internal inspections may be performed by quality assurance personnel. External audits are generally laboratory certification-related activities.

1. Internal

Periodically, the QA Officer (or designee) audits the laboratories and reports the results to the Division Manager (or laboratory director), laboratory managers, and unit supervisors.

2. External

State-certified laboratories are site visited every two years by auditors from the Environmental Laboratory Accreditation Program (ELAP) of the California Department of Health Services (CA DOHS). Accreditation is by scientific discipline or field of testing. Non-compliances with good laboratory practices are identified and reported as deficiencies and are subject to corrective action before accreditation is renewed.

Performance Audit

A performance audit is a review to evaluate the laboratory's analytical activities as well as the data produced by analysts. It verifies the ability of the laboratory to correctly identify and quantify compounds in unknown samples submitted by the auditing entity. The purpose of these audits is to determine the laboratory's capability to generate scientifically sound data.

1. Internal

Periodically, the QA staff submits unknown samples to most of the laboratories. These samples are usually from the inventory of previous Performance Evaluation (PE) samples from EPA. Analysis of these samples is also a corrective action requirement for Discharge Monitoring Report (DMR) and/or Water Pollution (WP) samples evaluated with "unacceptable results". The QA staff may also conduct intra- and inter-comparison studies.

2. External

- a. Mandatory Performance Evaluation (PE) Programs

- * Water Pollution QA Study Program (WP) serves a dual purpose. It satisfies EPA's wastewater testing laboratory requirements and meets one of ELAP's certification criteria. Test samples are analyzed for parameters listed under each field of testing on our

certifications and are specified in the WP Program following certified procedures. A laboratory can participate in a WP Study twice a year.

- * For the Microbiology Performance Evaluation (PE) Study, Drinking Water/Wastewater Enumeration is required for ELAP certification. Like all the other PE programs, the samples are acquired from NIST-approved vendors and analyses are done for certified analytes.

b. Voluntary PE Programs

These programs are performance based such as the interlaboratory calibration studies with EPA

Assessment of Precision and Accuracy

Data quality may be assessed in terms of precision, accuracy, representativeness, completeness, and comparability. The latter three are usually determined outside of the laboratory operations and with limited involvement of laboratory staff. These measures are not included in this section. The internal quality control measures (i.e., precision and accuracy) that are performed in the laboratory to evaluate data quality are described in this section.

Precision

Precision is the agreement among a set of replicate measurements without knowledge of the true value. It is the degree to which a measurement is reproducible. Precision, expressed as Relative Percent Difference (RPD), is determined for each laboratory unit by analyzing replicates of the same sample, a number of duplicate pairs, or matrix-spiked duplicate samples.

Accuracy

Accuracy is a measurement of how close the result is to the true value. Each laboratory unit establishes its accuracy of measurement by analyzing QC check samples (spiked samples, standard reference materials from a reliable source, etc). The results of the QC samples are correlated to documented, certified values. Results of spiked samples are calculated as Percent Recovery. Actual Percent Recovery is compared to established reference data. The degree of closeness of the QC check sample contributes to the general assurance that the accuracy of the data is within acceptable limits.

Corrective Action

Laboratory events and data that fall outside established quality acceptance criteria may require investigation or corrective action. The corrective action implemented depends on the type of analysis, the extent of the error, and whether the error can be determined and corrected. The purpose of the corrective action is to resolve the problem and to restore the system to proper operation. Investigative steps and corrective actions implemented are documented.

Corrective Action Procedures

1. The initial corrective action procedures may be handled at the bench level. The unit supervisor is immediately notified of the deviation. The analyst reviews the sample preparation for possible errors and checks the instrument calibration, calibration and spike solutions, instrument sensitivity, etc.
2. If the error cannot be resolved by the analyst, the unit supervisor has the responsibility of resolving the problem with assistance, if needed, from the laboratory manager and/or the QA Officer.
3. The corrective action adopted may be determined by the analyst, the unit supervisor, the laboratory manager, the QA Officer, or through a consensus. If needed, the final decision for corrective action rests with the laboratory manager after consultation with the QA Officer.
4. The unit supervisor shall maintain an accurate and up-to-date record of corrective actions taken in the unit. A corrective action report form (included herein as an attachment) is available for use.
5. The laboratory manager shall periodically review corrective action records and plan for system improvement by involving analysts, unit supervisors, and QA personnel.

General Guidelines for Initiating a Corrective Action

1. Identify/define the problem.
2. Assign responsibility for investigating the problem.
3. Investigate and determine the causes.
4. Develop corrective action to eliminate the problem.
5. Measure the effectiveness of the corrective action.
6. Analyst, unit supervisor, laboratory manager, and the QA Officer meet to review and evaluate the process, if necessary.
7. Document the process by filling out the Corrective Action Report Form.

APPENDIX I

Data Acquisition, Reduction, Validation, and Reporting Standard Operating Procedure (SOP)

The following procedures describe the data acquisition and entry process then the quality assurance and quality control procedures.

Data Acquisition

Both raw and calculated data are acquired in the laboratory by manual, electronic, or direct computer acquisition. Acquired data are properly and securely stored for the duration specified by regulatory agencies or the customer. Guidelines for documentation and recording of information are as follows:

- Manual (Hand-written) Data Entry
 - Data are entered directly into the notebook or worksheet with non-erasable ink.
 - Data entries are signed and dated by the analyst making the entry. If the entry is more than one page, each page is signed and dated.
 - Mistakes are canceled by drawing a line through the entry, entering the correct value, and signing and dating the correction. The use of correction fluid is not acceptable.
 - Blank pages or substantial portions of pages with no entries are marked with a large "X" to indicate that they were intentionally left blank.
- Direct Computer Acquisition
 - In EMD, the program/software used to generate results is prepared internally. A designated staff member of the Information & Control System Division (ICSD) at Hyperion has the responsibility of preparing the program and maintaining the supporting documents.
 - The laboratory relies on vendor-supplied information for the validity and integrity of instruments equipped with significant computer functions as an integral part of the system.

Data Reduction

Data reduction, where applicable, is described in specific SOP's. It involves reporting values with the appropriate significant figures in the concentration units established by the regulatory agency or the data user.

Review and Validation

Review

Data review is the process of comparing results to all available information, such as sample preparation and QC sample data, to evaluate the validity of the results. It supports the contention that the data are:

- Reasonable (experience with similar situations, common sense), and
- Capable of supporting a defensible decision.

The analyst and the unit supervisor (or designee) are responsible for reviewing the data relative to the following:

- Method blanks and QC sample
- Raw data
- Calculations
- Transcription

Validation

Data validation is the systematic procedure of reviewing data against a set of criteria to provide assurance of its validity before reporting the data. It is accomplished through routine examination of data collection, flow procedures, and QC sample results. It uses QC criteria to reject or accept specific data.

- Validation includes the following:
 - Dated and signed entries by analysts on the worksheets and logbooks used for all samples.
 - Use of QC criteria to reject or accept specific data.
 - Checking of LIMS data entry and reporting
- Validation Guidelines include the following:
 - Documentation of methods used and QC applied.
 - Maintenance performed on instruments.
 - Documentation of sample preservation, transport, and storage.
 - Review of QC sample data.

Data validation is performed, signed, and dated by the analyst, the unit supervisor (or designee), and where applicable, the laboratory manager.

Reporting

Data prepared for release to the Legal Reporting Unit are checked and approved by the unit supervisor (or designee) by the 5th of the following month for the previous month's data. The final report is prepared by the Legal Reporting Unit of EMD. The report is again scanned for missing data and outliers. Regulatory limitation calculations will be applied to the data set and exceedances clearly listed. If stations are out-of-compliance, accelerated monitoring will be indicated. Any regulatory required summary reports of source identification findings or sanitary surveys will be included. The report is signed by the Division Manager before distribution and may include the following:

- Sample ID used by the laboratory and the client (if available).
- Sample matrix type, description, and method number.
- The chemical/physical/biological parameters analyzed with the reported values and units of measurement.
- Data for all parameters reported with consistent number of significant figures.
- Results of QC samples, if appropriate.
- Footnotes referenced to specific data, if required, to explain reported values.
- If there are regulatory limits applicable to specific analyses, then limits are clearly notated and exceedances listed.
- Discussion on non-compliance data
- Report transmittal letter or memorandum identifying the person sending the report and the person(s) receiving the data.

APPENDIX J

Participating Organizations Contacts

<p>City of Los Angeles Penny Weiland, Co-chair penny.weiand@lacity.org (213) 485-3954 Seth Carr, Alternate co-chair seth.carr@lacity.org (213) 485-3961</p> <p>County of Los Angeles Daniel Dang, Co-chair P.E. ddang@dpw.lacounty.gov (626) 458-4359</p> <p>Long Beach Tom Leary Tom_Leary@longbeach.gov (562) 570-6023</p> <p>Signal Hill, Reach 1 Rep John Hunter jhunter@jlha.net (562) 802-7880</p> <p>Pasadena, Reach 2 Rep Sheila Kennedy skennedy@enfact.net (949) 721-1133</p> <p>Irwindale, Reach 2 Rep Ray Tahir rtahir@tecsenv.com (626) 396-9424</p>	<p>Downey, Reach 2 Rep Gerry Greene ggreene@downeyca.org (562) 904-7112</p> <p>Glendale, Reach 3 Rep Maurice Oillataguerre moillataguerre@ci.glendale.ca.us 818-548-3900</p> <p>Burbank, Reaches 4 & 5 Rep Rodney Andersen randersen@mail.ci.burbank.ca.us (818) 238-3931</p> <p>Hidden Hills, Reach 6 Rep Kevin Powers kevinpowers@caaprofessionals.com 310-257-2006</p> <p>Caltrans Bob Wu Robert_Wu@dot.ca.gov (213) 897-8636</p>
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APPENDIX K

Agencies Acknowledging CMP Submittal and Participation

Coordinated Monitoring Plan Participating Agencies	
City	Confirmation of Participation
Alhambra	YES
Arcadia	YES
Bell	YES
Bell Gardens	YES
Bradbury	YES
Burbank	YES
Caltrans	YES
Calabasas	NO
Carson	YES
Commerce	YES
Compton	YES
Cudahy	YES
Downey	YES
Duarte	YES
El Monte	YES
Glendale	YES
Hidden Hills	YES
Huntington Park	YES
Irwindale	YES
La Canada Flintridge	YES
Long Beach	YES
Los Angeles	YES
Lynwood	YES
Maywood	YES
Monrovia	YES
Montebello	YES
Monterey Park	YES
Paramount	YES
Pasadena	YES
Pico Rivera	YES
Rosemead	YES
San Fernando	YES
San Gabriel	YES
San Marino	YES
Sierra Madre	YES
Signal Hill	YES
South El Monte	YES
South Gate	YES
South Pasadena	YES
Temple City	YES
Vernon	YES
LA County-Unincorporated	YES